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Ammonium Sulfate and Bisulfate Formation in
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AMMONIUM SULFATE AND BISULFATE
FORMATION IN AIR PREHEATERS

Final Report

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ABSTRACT

Nitrogen oxide emissions from electric utility boilers may be reduced by 80-90% through the application of pollution control technology based on the selective catalytic reduction of nitrogen oxides with ammonia; however, some unreacted ammonia may be emitted from the control system. This study investigated the potential impact of these ammonia emissions on a combustion air preheater located downstream of a selective catalytic reduction system. A thermodynamic analysis was conducted which indicated that both ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) and ammonium bisulfate (NH_4HSO_4) could form in the intermediate and low temperature zones of an air preheater and that $(\text{NH}_4)_2\text{SO}_4$ was the thermodynamically favored reaction product. A kinetic analysis of the $\text{NH}_3\text{-SO}_3$ reactions was conducted which showed that NH_4HSO_4 is the first compound formed under the time-temperature histories found in an air preheater. This indicates that the reaction which forms NH_4HSO_4 from gaseous reactants is more rapid than the reaction which forms $(\text{NH}_4)_2\text{SO}_4$. Based on information collected during the study, five techniques were identified for minimizing the deposition of ammonium sulfates in an air preheater. A technical and economic evaluation of each solution was conducted and the results indicate that the use of available air preheater design options is the optimum technique for minimizing deposit formation.

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SECTION 1

SUMMARY

1.1 INTRODUCTION

Increased regulatory emphasis has been placed on reducing stationary source nitrogen oxide (NO_x) emissions. Currently, the two principal methods of controlling these emissions are combustion modifications and flue gas treatment. Combustion modifications are employed on new utility boilers and are generally capable of reducing NO_x emissions up to 50 percent. Flue gas treatment is a technology which is used commercially in Japan and it is currently being applied on a limited basis in the United States.

There are several flue gas treatment processes which are capable of reducing NO_x emissions by 90 percent. Of these, selective catalytic reduction is the most developed and appears to be the least expensive. Selective catalytic reduction employs a catalyst to promote the reaction of ammonia (NH_3) with NO_x to form molecular nitrogen and water.

One of the principal problems associated with this technology is the impact of unreacted or "leak" ammonia on equipment located downstream of the catalytic reactor. The downstream equipment may include the combustion air preheater, particulate collection equipment, and a flue gas desulfurization system.

This report presents the results of a study which examined the impact of unreacted ammonia on regenerative air preheaters. A separate investigation was conducted to examine impacts on baghouses, electrostatic precipitators, and flue gas desulfurization systems. The principal impact of ammonia emissions on air preheaters results from formation and deposition of ammonium sulfates in the

preheater. Reports from operating selective catalytic reduction systems in Japan indicate that the deposition can cause plugging and corrosion of the air preheater.

1.2 OBJECTIVES AND APPROACH

The overall goal of this study was to investigate the problems which result from deposition of ammonium sulfates in an air preheater. More specifically, the study had three major objectives. The first was to determine the conditions under which ammonium sulfates are expected to form. The second objective was to identify the factors which influence the formation of ammonium sulfates. The third objective was to identify and evaluate methods for preventing ammonium sulfate deposition/corrosion in air preheaters.

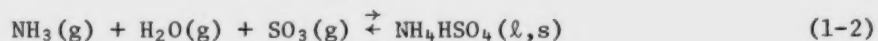
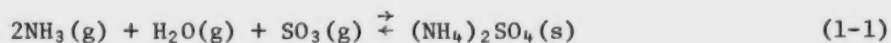
In order to identify conditions which favor the formation of ammonium sulfates, possible reactions were investigated and those of principal concern identified. A computer program based on the principle of free energy minimization was used to predict equilibrium concentrations of ammonium sulfate $((\text{NH}_4)_2\text{SO}_4)$ and ammonium bisulfate $(\text{NH}_4\text{HSO}_4)$ as a function of temperature and NH_3 and SO_3 concentrations in the flue gas.

Experimental data were then examined to determine what factors influenced the formation of the ammonium sulfates. Laboratory test results were compared to the expected equilibrium results and a kinetic model was developed to predict the formation and deposition of ammonium sulfates.

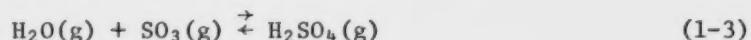
Finally, a number of solutions to the deposition problem were identified. A technical analysis of these solutions was completed and key economic factors quantified. Based on this evaluation the data needed to further define the feasibility and costs of the proposed solutions were identified.

1.3 RESULTS

The initial step in conducting this study required investigation of possible NH_3 reactions in the air preheater. Based on this analysis, the two principal reactions which can occur are illustrated by Equations 1-1 and 1-2.



Another related reaction which can affect the equilibria of the NH_3 reactions is shown in Equation 1-3.



Formation of H_2SO_4 tends to lower the concentration of SO_3 available for reaction with NH_3 (Equations 1-1 and 1-2). This, in turn, tends to reduce the temperature at which either $(\text{NH}_4)_2\text{SO}_4$ or NH_4HSO_4 will form. Of course, NH_3 can react with H_2SO_4 to form ammonium sulfates. However, these reactions occur at a lower temperature than the reactions of NH_3 with SO_3 . As a result, the formation temperatures for the reactions with H_2SO_4 define a lower limit for formation of $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 while the formation temperatures for the reactions with SO_3 define an upper limit.

Based on evaluation of NH_3 - SO_3 reactions, the compounds which can form in an air preheater are $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 . If only $(\text{NH}_4)_2\text{SO}_4$ forms, it will exist as a solid. This compound does not melt, it decomposes. If NH_4HSO_4 or both compounds form, the deposit may be either solid or liquid, depending on the composition and temperature (see Figure 3-1). Formation of liquid ammonium sulfates presents the most serious problem in terms of air preheater operation. The liquid deposits are corrosive and adhere to surfaces well. They also tend to collect or agglomerate particulates present in the gas stream and thus increase the potential for air preheater plugging.

Formation of solid ammonium sulfates should not present as serious a problem. The solid is not corrosive and it is not likely to adhere to surfaces and cause plugging of the preheater.

1.3.1. Analysis of Sulfate Deposition at Equilibrium Conditions

Once the principal NH_3 - SO_3 reactions were identified, a thermodynamic analysis was conducted to estimate the equilibrium concentrations of the ammonium sulfates as a function of temperature and the concentrations of NH_3 and SO_3 in the gas. The results of equilibrium calculations indicate that as gas containing NH_3 and SO_3 is cooled, $(\text{NH}_4)_2\text{SO}_4$ will form at higher temperatures than NH_4HSO_4 . While this may be true at equilibrium, it does not agree with experimental data which show that NH_4HSO_4 is the first compound formed from the reaction of gaseous NH_3 and SO_3 . Apparently the NH_4HSO_4 formation reaction occurs at a much more rapid rate than the $(\text{NH}_4)_2\text{SO}_4$ formation reaction.

The equilibrium calculations indicate that higher concentrations of NH_3 and SO_3 result in higher formation temperatures for both $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 . These calculations also show that the formation reactions can occur in a narrow temperature range. For example, the temperature drop required to permit 90 percent reaction of NH_3 and SO_3 is approximately 30°C for the cases examined in this study.

Another significant result of the equilibrium calculations is that the estimated formation temperatures for $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 were lower than those predicted by investigators in Japan. It appears that previous investigators' thermodynamic analyses of these reactions neglected to include the sulfuric acid formation reaction (Equation 1-3). In the temperature range of product formation, over 90 percent of the SO_3 present in the gas will exist as H_2SO_4 vapor. This tends to lower the product formation temperatures since there is effectively less SO_3 available for reaction (Equations 1-1 and 1-2).

1.3.2 Development of Kinetic Model for Sulfate Deposition Prediction

Once the equilibrium calculations were completed, a kinetic analysis of $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 formation and deposition was conducted. This analysis involved development and application of a kinetic model of the deposition problem. Based on experimental data, it was assumed that NH_4HSO_4 is the only deposition product for an initial NH_3/SO_3 mole ratio of 1 to 1 and that the rate of the chemical reaction which forms NH_4HSO_4 is very rapid. The resultant model predicts deposition based on the rates of simultaneous heat and mass transfer in a heat exchanger.

The kinetic model was applied to laboratory data and the predicted results were found to be consistent with experimental data. This indicates that the assumptions used in developing the model are valid: at an NH_3/SO_3 mole ratio of 1 to 1, the principal reaction product formed is NH_4HSO_4 and the rate of the NH_4HSO_4 formation reaction is rapid. In other words, the amounts of NH_3 , SO_3 and NH_4HSO_4 present in an air preheater can be approximated by equilibrium calculations since the rate of chemical reaction is very rapid.

The applicability of the model also identifies the mechanism for deposit formation. Based on Radian's kinetic analysis, it appears that NH_4HSO_4 can form in an air preheater as "condensate" on the surface of the preheater or as an aerosol. Any aerosol formed can either deposit on the surface or be carried through the preheater. The principal factor which determines the amount of NH_4HSO_4 that condenses on the surface and the amount that forms as an aerosol is the relative temperature of the preheater surface and the flue gas being cooled. The major factor which controls aerosol deposition cannot be quantified. However, for the laboratory experiments which were examined, the aerosol deposition appeared to increase with increasing gas velocity.

1.3.3 Techniques for Minimizing Preheater Sulfate Deposition

Based on the results of the thermodynamic and kinetic analyses, an evaluation of air preheater design and operation, and an examination of SCR operation, five techniques were identified for minimizing the deposition of ammonium sulfates in an air preheater. These techniques involve modification of (1) air preheater design and/or operation, or (2) SCR system design. The following discussion examines the five techniques for minimizing deposit formation and summarizes the advantages and disadvantages of each.

Modification of Air Preheater Design/Operation--

Four techniques identified for minimizing the impacts of deposit formation require modification of air preheater design or operation. These techniques are:

- Use of Available Air Preheater Design Options
- Heat Cleaning of the Air Preheater
- Flue Gas Recirculation for Selective Formation of $(\text{NH}_4)_2\text{SO}_4$
- Increased Air Preheater Operating Temperature

Each of these techniques is discussed below.

Use of available air preheater design options--One method of limiting the impact of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposit formation is to make use of available options when specifying an air preheater design. Specifically, this includes:

- Both hot- and cold-end soot blowers
- Increased soot-blowing frequency
- Increased soot blowing steam pressure
- Provisions for in-service water washing of the preheater

- Use of corrosion resistant material in both the intermediate and low temperature zones of the preheater
- Use of combined intermediate and low temperature heat transfer elements

Most of these options will increase the annualized costs of air preheater operation. However, the effect of employing the options will be to virtually eliminate any impact associated with $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition. Use of combined heat transfer elements, increased soot blowing intensity, and in-service washing should prevent forced boiler outages due to plugging of the preheater. The use of corrosion resistant material in the preheater should permit reliable air preheater operation over the life of the unit.

Heat Cleaning of the Air Preheater--The fact that $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposits decompose at elevated temperatures provides the basis for a second solution to the deposition problem. This solution, termed "heat cleaning", requires that the operating temperature in the preheater be elevated to the point where $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 will rapidly decompose (350 to 450°C). Periodic cleaning using this technique should help prevent deposit build-up.

Use of the heat cleaning technique has several drawbacks. First, the elevation of preheater temperatures will result in a temporary decrease in boiler efficiency. Second, depending on the method of heat cleaning, the flue gas which exits the preheater may need to be cooled to prevent damage to the downstream equipment due to the high temperature of the gas. Cooling the gas may also be required to recondense the $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ so these compounds can be collected in particulate control equipment. Third, if temperature gradients greater than those encountered during normal operation of the preheater occur during heat cleaning, differential expansion can damage the preheater. Finally, heat cleaning will not be effective in removing deposits of $\text{NH}_4\text{-Fe-SO}_4$ compounds and $\text{NH}_4\text{-fly ash-SO}_4$ compounds which can form in the preheater.

The most promising technique for implementing heat cleaning involves eliminating the flow of air to a preheater while simultaneously reducing the flue gas flow rate to about 10 percent of design flow. This will result in raising the air preheater temperature to the entering flue gas temperature ($\sim 350^{\circ}\text{C}$) with a minimum of problems. Since no air flows through the preheater during this period, differential expansion of the preheater wheel should not present a problem. Also, operation at a reduced flue gas flow will minimize the decline in boiler efficiency, and it may not be necessary to cool the flue gas exiting the preheater with dilution air. The principal problem with this technique appears to be the requirement for isolation of the preheater which may necessitate a temporary reduction in boiler load.

It should be noted that no data are available which indicate if heat cleaning will work or how effective it will be. This solution is based on theoretical considerations and requires experimental work to substantiate its feasibility. In ranking the technical feasibility of this solution, it is considered as possible but not proven.

Flue gas recirculation for selective formation of $(\text{NH}_4)_2\text{SO}_4$ --The results of the thermodynamic analysis have identified several useful facts concerning the formation of ammonium sulfates. First, $(\text{NH}_4)_2\text{SO}_4$ forms at higher temperatures than NH_4HSO_4 and in pure form exists only as a solid. Second, at 20°C below the initial formation temperature, the $(\text{NH}_4)_2\text{SO}_4$ formation reaction can proceed to approximately 80 percent completion. By modification of the air preheater design, it may be possible to exploit these facts to selectively form $(\text{NH}_4)_2\text{SO}_4$ and thereby minimize deposit formation.

One potential technique for selectively forming $(\text{NH}_4)_2\text{SO}_4$ employs flue gas recirculation from downstream of the air preheater to cool hot flue gas in a reaction chamber. Temperatures are controlled in the chamber so $(\text{NH}_4)_2\text{SO}_4$ is formed, but no NH_4HSO_4 forms. The solid $(\text{NH}_4)_2\text{SO}_4$ should then pass through the preheater and be collected by particulate control equipment.

Flue gas recirculation was identified as a possible solution to the deposition problem based strictly on the results of Radian's thermodynamic analysis of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ formation. However, there are factors which make the feasibility of this solution uncertain. First, there are no data on the rate at which $(\text{NH}_4)_2\text{SO}_4$ forms from gas phase reactants. All experimental data, including analysis of air preheater deposits, indicate that NH_4HSO_4 is the first product to form from gaseous reactants. The results of Radian's kinetic analysis confirms that the NH_4HSO_4 formation reaction occurs very rapidly but the $(\text{NH}_4)_2\text{SO}_4$ formation rate could not be determined. Therefore, it may be impossible to selectively form $(\text{NH}_4)_2\text{SO}_4$ with a realistically sized reaction chamber residence time (i.e., 1 to 2 sec.).

A second problem associated with flue gas recirculation is one of the process control. Changes in fuel sulfur content or excess air to the boiler may change the SO_3 concentration while changes in flue gas flowrate and NO_x concentration can change the concentration of NH_3 which is emitted from the reactor. If the air preheater is designed for one range of NH_3 - SO_3 concentrations and a significant change in these concentrations occurs, it will be difficult to control the system so formation of $(\text{NH}_4)_2\text{SO}_4$ is limited to the reaction chamber and NH_4HSO_4 formation is prevented. The principal reason for this is that both NH_3 and SO_3 must be measured continuously in order to adjust the recirculation rate to the reaction chamber and thus control formation of $(\text{NH}_4)_2\text{SO}_4$. Unfortunately, both NH_3 and SO_3 are difficult to measure on a continuous basis.

The problems associated with use of flue gas recirculation represent significant technical obstacles. No data are available to indicate whether it is possible to selectively produce $(\text{NH}_4)_2\text{SO}_4$. In addition, the control problems associated with changing NH_3 - SO_3 concentrations will be difficult to resolve. Therefore, the technical feasibility of using flue gas recirculation to prevent deposit formation is considered to be low.

Increased air preheater operating temperature--The most direct technique for eliminating the deposition of ammonium sulfates is to increase the air preheater operating temperature above the temperature at which NH_4HSO_4 forms. This should minimize plugging and corrosion since any $(\text{NH}_4)_2\text{SO}_4$ which forms and/or deposits will be non-corrosive. These deposits will occur in the extreme cold-end of the preheater and should be easily removed by soot blowing.

Modification of the air preheater design to permit operation at a higher temperature should be relatively simple. The principal change required is a reduction in thermal efficiency of the preheater. Efficiency can be reduced by reducing the size of the preheater so the cold-end temperature is above the NH_4HSO_4 formation temperature.

The principal impact of increasing the cold-end metal temperature will be to decrease boiler efficiency. In addition, there may be some impacts on downstream equipment and possibly an environmental impact due to gas phase NH_3 and SO_3 emissions. For these reasons, it will be necessary to cool the flue gas exiting the preheater below the NH_4HSO_4 formation temperature with ambient air. This will minimize impacts on downstream equipment. It will also result in production of solid $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ which can be collected in an ESP.

Modification of SCR Design/Operation--

Modification of air preheater design and operation represents one general approach to solving the $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition problem. A second approach to solving this problem is to modify the SCR system design. The intent of modifying the SCR system is to reduce the NH_3 emissions from the reactor, thereby reducing the formation of ammonium sulfates in the preheater. In various SCR operations, NH_3 concentrations below 10 ppm have been shown to minimize deposit formation.

There is basically one way to modify the SCR system so that the NH_3 emissions are reduced and a specified level of NO_x removal is achieved. This technique requires the use of additional catalyst so that the NH_3 injection rate can be lowered while maintaining the desired NO_x removal level, thus reducing the NH_3 emissions.

Increased quantity of catalyst--The design of an SCR system is influenced by a trade-off between the quantity of catalyst in the reactor, the NH_3 injection rate, and the NO_x removal efficiency of the system. The specification of each design parameter will be determined by its impact on the annual costs of operating the system, regulatory requirements on NO_x emissions, and the requirement for preventing excessive NH_3 emissions. Without regard for system costs, these parameters can be adjusted to maintain a constant NO_x removal efficiency while minimizing NH_3 emissions.

By increasing the quantity of catalyst while simultaneously reducing the NH_3 injection rate, the NH_3 emissions can be reduced. This relationship is quantified in Table 1-1. As shown, NH_3 emissions for the base case are 30 ppm. Approximately 30 percent additional catalyst is required to reduce NH_3 emissions to 10 ppm while 70 percent more catalyst should eliminate NH_3 emissions almost entirely. The estimated minimum NH_3/NO_x mole ratio is 0.92.

TABLE 1-1. EFFECT OF INCREASED CATALYST ON NH_3 EMISSIONS*

Case	Base	1	2	3
Relative Catalyst Amount	1.0	1.10	1.31	1.71
NH_3/NO_x for 90% Removal	1.0	0.98	0.95	0.92
NH_3 Emissions (ppm)	30	20	10	0

*Details of how these values were determined are contained in Appendix C.

The most significant impact of increasing the amount of catalyst in the reactor will be to increase the costs of operating the SCR system. This results from the requirement for replacing the catalyst at regular intervals. Increasing the amount of catalyst will also result in a slight reduction in the NH_3 consumption for the system. No significant energy penalties will result from increasing the catalyst quantity, although SCR reactor pressure drop will increase somewhat.

1.3.4 Estimated Costs for Proposed Solutions to the $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ Deposition Problem

A technical and economic analysis of the five solutions was completed using a 500 MW, coal-fired power plant as a basis. Specific details of the base-case plant are presented in Table 1-2. As shown, capital and annualized costs are for a new installation operating 7000 hrs per year.

The results of the technical and economic analysis of the five techniques for minimizing the impacts of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition are summarized in Table 1-3. Based on these results it appears that use of available air preheater design options is the preferred solution to the deposition problem considering both technical and economic factors. However, the solutions with lower technical feasibility could result in lower annual costs and thus merit further investigation. The solutions which employ modification of SCR design and the use of increased air preheater operating temperatures do not appear to be economically competitive with the other proposed solutions. Specific details of how the costs presented in Table 1-3 were developed are presented in Section 6.0 and Appendix C.

TABLE 1-2. BASIS FOR ESTIMATING INCREMENTAL COSTS
OF PROPOSED SOLUTION

Parameter	Base Value
<u>Boiler Characteristics</u>	
• Size	500 MWe
• Thermal Efficiency	88%
• Number of Air Preheaters	2
• Flue Gas Flowrate	620 kg/sec (82,000 lb/min)
• Heat Rate	9.49 MJ/kWh (9000 Btu/KWh)
• Operating Factor	7000 hrs/yr
<u>SCR Characteristics</u>	
• NO _x Removal Efficiency	90%
• NH ₃ /NO _x Mole Ratio	1.0
• NH ₃ Emissions	30 ppm
<u>Air Preheater Characteristics</u>	
• Type/Size	Ljungstrom ¹ Tri-Sector/Size 31
• Number of Soot Blowers	1 per air preheater (cold-end)
• Soot Blowing Frequency	3 times per day
• Soot Blowing Steam Pressure	1.48 MPa (200 psig)
<u>Cost Characteristics</u>	
• Year	1979 Capital/1980 Annualized
• Fuel Cost	\$2.37/GJ (\$2.5/10 ⁶ Btu)
• Air Preheater Capital Cost	\$2,600,000
• Type of Installation	New
• Capital Charge Rate	14.6%

¹Mention of trade names does not constitute endorsement or recommendation by the EPA.

TABLE 1-3. TECHNICAL AND ECONOMIC RANKING OF PROPOSED SOLUTIONS
TO THE $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ DEPOSITION PROBLEM

Solution	Relative Technical Feasibility ¹	Estimated Incremental First Year Annualized Costs (1000's)
Air Preheater Design Options	Intermediate	452
Heat Cleaning	Low	271
Flue Gas Recirculation		
- Single Preheater	Low	857
- Split Preheater	Low	(198)
Increased Cold-End Metal Temperature	High	3098
Increased Catalyst Decreased NH_3/NO_x	Intermediate	3668 ^{2,3}

¹These are somewhat subjective and based on engineering judgement.

²This cost is based on reducing NH_3 emissions to approximately 10 ppm.

³Assumes a 1-year catalyst life (current vendor guarantee for coal-fired applications).

1.4 CONCLUSIONS

The following discussion presents conclusions based on the work performed during this study. For the most part, the information obtained during the course of the study is summarized in this report and serves as background for the conclusions presented here. The major conclusions of this study are:

- NH_3 leakage from SCR reactors can present a problem for an air preheater located downstream of the reactor. However, operating experience indicates that NH_3 concentrations below 10 ppm at the air preheater entrance do not result in serious deposition problems. This is probably due to the fact that at low NH_3 concentrations, NH_4HSO_4 forms in the cold-end of the preheater where existing soot blowing equipment is more effective in removing deposits.
- The effects of the deposition problems are limited to plugging of the preheater and corrosion of preheater materials in the intermediate temperature zone. The ability of the preheater to transfer heat should not be impaired by deposit build-up. In addition, normal corrosion in the extreme cold-end of the preheater will be reduced due to neutralization of $\text{SO}_3\text{-H}_2\text{SO}_4$ by NH_3 .
- No significant environmental problems will result from washing deposits from the air preheater. The NH_3 levels in the preheater wash water will be lower than those typically encountered in power plant metal cleaning wastes. A slight increase in waste treatment costs may result due to increased volume of wash water. The magnitude of this cost increase will be site specific and depends on the method of waste water treatment employed.
- The problems associated with deposition of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ can be minimized or eliminated by several possible techniques. The principal impact of implementing these techniques will be to change the annual costs for SCR operation. Table 1-4 presents the annualized costs for various solutions to the deposition problem as a percentage of the annual revenue requirements for SCR. As shown, the cost impact of the solutions range from a 1.6 percent reduction to a 30 percent increase in annualized costs.

TABLE 1-4. ESTIMATED INCREASE IN SCR ANNUALIZED COSTS
FOR PROPOSED SOLUTIONS TO THE $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ DEPOSITION PROBLEM

Solution	Increase in SCR Annualized Costs (%)
Air Preheater Design Options	3.7
Heat Cleaning	2.2
Flue Gas Recirculation	
- Single Preheater	7.0
- Split Preheater	(1.6)
Increased Cold-End Metal Temperature	25.4
Increased Catalyst/Decreased NH_3/NO_x	30.0

SECTION 2

INTRODUCTION

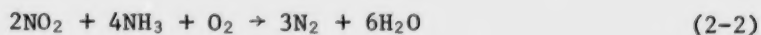
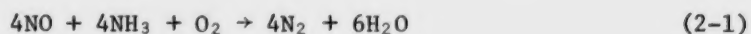
In 1971 the U.S. Environmental Protection Agency (EPA) formulated New Source Performance Standards (NSPS) designed to limit nitrogen oxide emissions from stationary combustion sources. This standard has proven relatively easy to comply with through modification of boiler design and operation (combustion modifications).

On June 11, 1979 EPA revised the NSPS for electric utility steam generating units. The revised standards call for a further reduction in the NO_x emission rates based on improvements in combustion modification technology. In addition, EPA is studying the need for a short-term ambient NO_x standard. In certain air quality control regions, this could require a reduction in NO_x emission rates beyond those achievable with combustion modifications.

Currently there are many processes designed to limit stationary source NO_x emissions. Of these, only selective catalytic reduction (SCR) has commercially demonstrated the capability of limiting NO_x emissions from stationary sources by 90 percent or more. SCR processes have been developed in Japan and are used extensively (over 40 commercial installations) to meet Japan's stringent NO_x emission standards.¹

For a utility application of SCR, a catalytic reactor is generally located between the economizer and air preheater sections of the boiler. At this point the flue gas temperature ranges from 300 to 400°C (570-750°F) which

is suitable for the NO_x reduction reactions to occur rapidly. Ammonia is injected into the flue gas upstream of the catalyst and reacts with NO_x on the catalyst surface to form elemental nitrogen and water. The overall reactions can be represented by Equations 2-1 and 2-2.

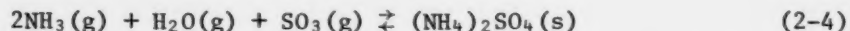


The actual mechanism of NO_x reduction is more complex than illustrated by these equations and it is not fully understood at this time.

Although SCR systems have undergone extensive commercial development in Japan, an unresolved issue is that of ammonia emissions from the process and the impact of these emissions on equipment located downstream of the catalytic reactor. Such equipment can include air preheaters, flue gas desulfurization systems and particulate removal devices.

A related technology which has similar problems is selective non-catalytic reduction (SNR). This technology also employs NH_3 as a reductant. The NH_3 is injected into a high temperature zone (900 to 1000°C) in the boiler where the rate of the NH_3 - NO_x reactions (Equations 2-1 and 2-2) is rapid. SNR is generally not capable of reducing NO_x emissions as efficiently as SCR, in terms of both the percentage of NO_x reduced and the amount of ammonia required to reduce a given quantity of NO_x .

This study addresses the impact of ammonia emissions on the operation of air preheaters located downstream of SCR systems (data from SNR systems will also be discussed). In particular, the formation and deposition of ammonia sulfates in air preheaters were investigated. Ammonium sulfate salts can form in the air preheater due to reaction of ammonia, sulfur trioxide, and water present in the flue gas as illustrated by Equations 2-3 and 2-4.



The direction in which these reactions proceed is dependent on the flue gas temperature and the concentrations of the reactants. At a given flue gas concentration, the formation of the solid sulfate and liquid bisulfate will occur as the flue gas is cooled. For typical concentrations of NH_3 (10 to 30 ppm) and SO_3 (5 to 10 ppm) downstream of an SCR unit, the approximate formation temperatures of $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 range from 195° to 210°C and 165° to 180°C, respectively. Typical air preheater operating temperatures for the flue gas range from over 300°C at the inlet to about 150°C at the air preheater outlet². Obviously, the thermodynamics of the formation reactions indicate that some $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 can form in the air preheater.

The formation and deposition of ammonium sulfates in air preheaters has been observed downstream of SCR and SNR systems³. Deposits have also formed during tests of fly ash conditioning with ammonia for improved ESP performance (Section 4.2). The deposition of ammonium sulfates has caused plugging of air preheater gas passages and corrosion of the preheater. This can impair the operation and reliability of the boiler.

This study investigated the chemistry of the NH_3 - SO_3 reactions and the design and operating principles of commercial air preheaters. Its goal was to identify possible solutions to the plugging and corrosion problems which result from deposition of ammonium sulfates in air preheaters.

As background for this study, Dr. Jumpei Ando (Professor of Engineering, Chuo University, Tokyo, Japan) prepared a study of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ formation and problems associated with formation of these compounds. Ando's work

included a survey of selected SCR and SNR installations, results of laboratory work on deposit formation and corrosion, and results of chemical analyses of actual air preheater deposits. Information from Dr. Ando's work is incorporated as appropriate with the results of Radian's investigation of this problem.

Program Objectives and Approach

This program had three major objectives. The first was to determine the conditions under which ammonium sulfates are expected to form. The second objective was to identify the factors which influence the formation of ammonium sulfates. The third objective was to identify and evaluate methods for preventing ammonium sulfate deposition/corrosion in air preheaters.

In order to identify conditions which favor the formation of ammonium sulfates, possible reactions were investigated and those of principal concern identified (Equations 2-3 and 2-4). A computer program based on the principle of free energy minimization was used to predict equilibrium concentrations of ammonium sulfate and ammonium bisulfate as a function of temperature and NH_3 and SO_3 concentrations in the flue gas. This approach is discussed in Section 5.1 and Appendix A.

Experimental data were then examined to determine what factors influence the formation of the ammonium sulfates. Laboratory test results were compared to the expected equilibrium results and a kinetic model was developed to predict the formation and deposition of ammonium sulfates. The results of this work are discussed in Section 5.2 and Appendix B.

Finally, a number of solutions to the deposition problem were identified. A technical analysis of these solutions was completed and key economic factors quantified (Section 6). Based on this evaluation the data needed to further define the feasibility and costs of the proposed solutions were identified.

Report Organization

This report is organized to address each of the study objectives. In addition, the report contains a summary of available data on $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition and related issues (e.g., laboratory studies of corrosion by NH_4HSO_4). Section 3 presents a description of the $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition problem. This includes a discussion of $\text{NH}_3\text{-SO}_3$ reactions and chemistry, air preheater design and operation, preheater plugging and corrosion, and environmental considerations. Section 4 contains a summary of actual experience with air preheater plugging and corrosion by $\text{NH}_3\text{-SO}_3$ compounds. Section 5 presents the thermodynamic and kinetic analyses of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ formation and deposition including a discussion of results. In Section 6, possible solutions to the deposition problem are defined and evaluated.

SECTION 3

PROBLEM DEFINITION

Selective catalytic reduction technology has been the subject of extensive development work in Japan, having been applied commercially at more than 40 installations. However, some problems still exist with the application of SCR. One of these problems results from unreacted NH_3 being emitted from the reactor. This "leak" NH_3 can react with SO_3 present in the flue gas to form $(\text{NH}_4)_2\text{SO}_4$ or NH_4HSO_4 which can then deposit as a solid and/or liquid in equipment located downstream of the reactor. In particular, deposition of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ has resulted in plugging and corrosion of air preheaters.^{1,3}

The problem of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition has several aspects which must be considered. The chemistry of the NH_3 - SO_3 reactions must be examined and the principal causes of deposit formation identified. The potential for subsequent reaction of deposits with air preheater materials must also be considered since this can result in corrosion and ultimately reduce the useful life of the air preheater. In addition, the impact on operation and maintenance of the air preheater must be considered. This includes any changes in performance, increased boiler outage time due to plugging, and the time, equipment and manpower required to remove deposits from the air preheater. Finally, the environmental impacts associated with $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition must be considered. This would principally involve handling and treatment of water used to wash deposits from the air preheater.

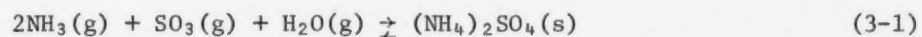
Each aspect of the $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition problem must be defined before a solution can be identified. This section presents an introductory discussion of the important aspects of the problem. The discussion is based

on the results of a study of the chemistry of $\text{NH}_3\text{-SO}_3$ reactions, a survey of previous experience with air preheater operation and plugging, laboratory work on corrosion by NH_4HSO_4 , and examination of other relevant experience. Section 4.0 presents a detailed summary of actual air preheater operating experience involving $\text{NH}_3\text{-SO}_3$ compound deposition while Section 5.0 contains a detailed discussion and analysis of the physical and chemical causes of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ formation. In Section 6.0 potential solutions to the $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ problem are offered and discussed.

3.1 CHEMICAL FACTORS AFFECTING $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ FORMATION AND DEPOSITION

Experience at SCR and SNR installations has demonstrated that NH_3 and SO_3 can react and deposit in air preheaters. Chemical analysis of the deposits indicates that the principal reaction products are $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 . Other components in the deposits include corrosion products ($\text{NH}_4\text{-Fe-SO}_4$ compounds) and fly ash (Ca, Si, and Al compounds).³ This section presents a discussion of the reactions which can occur in an air preheater and identifies the chemical factors which influence deposit formation.

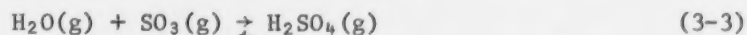
The $\text{NH}_3\text{-SO}_3$ reactions which can take place in an air preheater are illustrated by Equations 3-1 and 3-2.



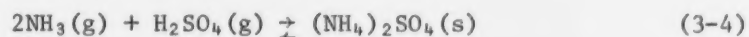
These reactions can occur as a gas containing NH_3 , SO_3 , and H_2O is cooled. For a flue gas stream, the exact temperature at which solid/liquid products begin to form or "condense" depends on the reaction product(s) formed and on the concentrations of NH_3 , SO_3 , and to a lesser degree, H_2O . In general, as the concentrations of reactants in the gas increase, the temperature at which deposits will form also increases. In terms of air preheater operation, this means that an increase in NH_3 or SO_3 concentration will increase the possibility of deposit formation. A detailed analysis of the relationship

between NH_3 and SO_3 concentrations and formation temperature is presented in Appendix A.

Another reaction which occurs as the gas is cooled is represented by Equation 3-3.



Formation of H_2SO_4 tends to lower the concentration of SO_3 available for reaction with NH_3 (Equations 3-1 and 3-2). This, in turn, tends to reduce the temperature at which either $(\text{NH}_4)_2\text{SO}_4$ or NH_4HSO_4 will form. Of course, NH_3 can react with H_2SO_4 as illustrated by Equations 3-4 and 3-5.



However, these reactions occur at a lower temperature than the reactions defined by Equations 3-1 and 3-2. As a result, the formation temperature for the reactions shown in Equations 3-4 and 3-5 define a lower temperature limit for formation of $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 while the formation temperature for Equations 3-1 and 3-2 define an upper limit. In most cases, predicted formation temperatures will fall between the two extremes due to the reaction shown in Equation 3-3.

Ammonia can react with other flue gas components to form solid products. A list of potential reactions is presented in Table 3-1. These reactions and their products were not considered in this study since their formation temperatures (for typical flue gas concentrations) are below the temperatures encountered in air preheater operation.

TABLE 3-1. POTENTIAL REACTIONS OF AMMONIA WITH FLUE GAS COMPONENTS

Component	Possible Reaction
CO ₂ (g)	$2\text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons (\text{NH}_4)_2\text{CO}_3(\text{s})$
	$\text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{NH}_4\text{HCO}_3(\text{s})$
SO ₂ (g)	$2\text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{g}) + \text{SO}_2(\text{g}) \rightleftharpoons (\text{NH}_4)_2\text{SO}_3(\text{s})$
	$\text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{g}) + \text{SO}_2(\text{g}) \rightleftharpoons \text{NH}_4\text{HSO}_3(\text{s})$
NO(g)	$2\text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) + 2\text{NO}(\text{g}) \rightleftharpoons 2\text{NH}_4\text{NO}_2(\text{s})$
NO ₂ (g)	$2\text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) + 2\text{NO}_2(\text{g}) \rightleftharpoons 2\text{NH}_4\text{NO}_3(\text{s})$
HCl(g)	$\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightleftharpoons \text{NH}_4\text{Cl}(\text{s})$

Based on evaluation of NH₃-SO₃ reactions, the compounds which can form in an air preheater are (NH₄)₂SO₄ and NH₄HSO₄. If only (NH₄)₂SO₄ forms, it will exist as a solid. This compound does not melt, it decomposes. If NH₄HSO₄ or both compounds form, the deposit may be either solid or liquid. This depends on the deposit composition and the temperature as shown in Figure 3-1. For example, if the NH₃/H₂SO₄ mole ratio of a deposit is 1.2 and the deposit exists at 225°C (Area D), the deposit is a liquid solution of (NH₄)₂SO₄ and NH₄HSO₄. If this same deposit is cooled to 150°F (Area C), it exists as a liquid solution of (NH₄)₂SO₄ and NH₄HSO₄ in equilibrium with solid (NH₄)₂SO₄. If it is further cooled (Area A), the deposit would be a mixture of solid (NH₄)₂SO₄ and NH₄HSO₄.^{1,4}

The chemical composition of ammonium sulfates which deposit in an air preheater will depend on several factors including the relative amounts of NH₃ and SO₃ in the flue gas and the time-temperature history of the flue gas as it passes through the air preheater. Based on the results of Radian's thermodynamic analysis of NH₃-SO₃ reactions, the formation of (NH₄)₂SO₄ is favored over NH₄HSO₄. This means that as a gas containing NH₃, SO₃, and H₂O is cooled, (NH₄)₂SO₄ should be the first compound to form. However, the results of Radian's kinetic analysis indicates that under the time-temperature conditions found in an air preheater, NH₄HSO₄ will form first. Apparently the reaction rate for formation of NH₄HSO₄ is more rapid than that for

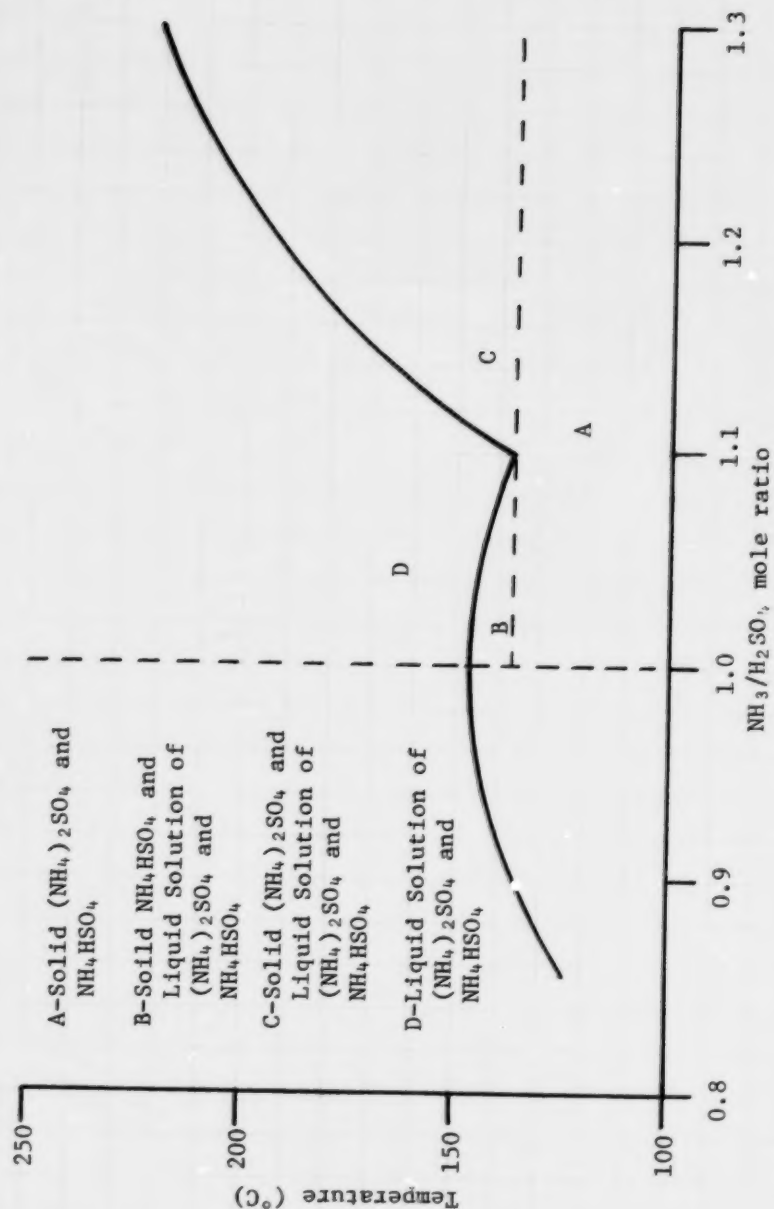
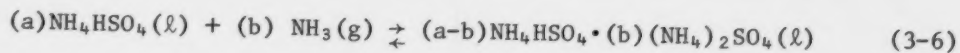


Figure 3-1. Melting point of NH₃/H₂SO₄ mixtures as a function of composition.

formation of $(\text{NH}_4)_2\text{SO}_4$ from gaseous reactants. It appears that significant quantities of $(\text{NH}_4)_2\text{SO}_4$ will form in an air preheater only if an excess of NH_3 exists to react with NH_4HSO_4 as shown in Equation 3-6.



The ratio of NH_3 to SO_3 in deposits is not equal to the ratio of NH_3 to SO_3 in the flue gas. It depends on the location of the deposits in the preheater since the local concentrations of NH_3 and SO_3 can vary significantly due to depletion by chemical reaction and differences in the diffusion rates of NH_3 and SO_3 .

Dr. Ando conducted laboratory experiments which examined deposit composition as a function of distance through a heat exchanger. In these tests, the deposit composition was relatively independent of the ratio of NH_3 to SO_3 at the entrance to the heat exchanger but was more dependent on this ratio further into the heat exchanger.

Based on Ando's experiments, it appears that the NH_3 to SO_3 ratio in most deposits can be maximized at 2.0 by providing an excess of NH_3 at the inlet to the preheater (i.e., NH_3/SO_3 mole ratio >2.0). This would result in deposits containing solid, non-corrosive $(\text{NH}_4)_2\text{SO}_4$. However, increasing the NH_3 concentration at the preheater inlet has the adverse effects of increasing the temperature at which deposits will form and increasing the quantity of deposits which can form.

3.2 THE EFFECT OF AIR PREHEATER DESIGN AND OPERATION ON DEPOSIT FORMATION

Early experience with corrosion and plugging of air preheaters resulted from condensation of H_2SO_4 vapor on the metal surfaces in the preheater. In coal-fired applications, fly ash deposits on the acid wetted surface, physically absorbs and then chemically reacts with and neutralizes the acid forming a solid deposit or scale. In this situation, corrosion of the preheater is not a serious problem and plugging can be minimized by the use of soot blowing

equipment. In oil-fired applications, there is little ash and acid corrosion can be severe.

The deposition of $\text{NH}_3\text{-SO}_3$ compounds is somewhat analogous to the H_2SO_4 condensation problem. Liquid NH_4HSO_4 or a solution of $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 can condense and deposit in the air preheater. Formation of solid $(\text{NH}_4)_2\text{SO}_4$ should not present a problem since the solid should not adhere to the surface as readily as a liquid. Liquid $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposits are similar to H_2SO_4 deposits. In coal-fired applications, they tend to collect fly ash particles and to react with both the fly ash and the metal surface in the air preheater to form a solid deposit. In oil-fired applications, ammonium sulfates would be expected to be more corrosive since no fly ash is present to neutralize those deposits.

In order to provide a basis for understanding the $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition problem, the design and operation of air preheaters must be examined. The following discussion presents some important aspects of preheater design and identifies how $\text{NH}_3\text{-SO}_3$ compound formation impacts preheater operation.

3.2.1 Air Preheater Design Fundamentals

There are two basic air preheater designs in use; recuperative and regenerative. Recuperative air preheaters are the tubular type in which flue gas flows through the tubes and combustion air flows through a surrounding shell. Heat is transferred from the flue gas through the tube walls to the combustion air. Recuperative air preheaters are typically large units relative to regenerative preheaters, requiring approximately 3 times the space for a given capacity. Another important difference between recuperative and regenerative air preheaters is that recuperative preheaters operate with lower metal temperatures for a given heat transfer rate.^{3,5}

There are two major types of regenerative air preheaters; Rothemuehle and Ljungstrom. However, the principal of operation is the same for both types. In a regenerative air preheater, heat is absorbed from the flue gas by metal heat transfer elements. These metal elements are then exposed to the combustion air where they release the heat absorbed from the flue gas. Subsequently, the elements are reexposed to the flue gas and the cycle is repeated. In the Rothemuehle type air preheater, the heat transfer elements are fixed and the air duct is rotated. In the Ljungstrom type preheater, the duct work is stationary but the metal heat transfer elements are rotated. Both designs result in the elements being alternately exposed to flue gas and then combustion air.

Currently, most new industrial boiler designs specify recuperative air preheaters while essentially all the new utility boiler designs specify the regenerative type. The discussion presented here and the analysis in Section 6 will focus on the regenerative type of air preheaters. The reason for emphasizing regenerative preheaters is that the initial application of SCR technology is expected to be limited to utility and large industrial boilers which almost exclusively use regenerative air preheaters.

In a regenerative air preheater, the temperature of the metal heat transfer elements change continuously as they are alternately exposed to flue gas and then combustion air. In addition, the temperature varies through the depth of the preheater. Figure 3-2 presents a typical temperature profile for a regenerative (Ljungstrom type) air preheater. The center line represents the average metal temperature as a function of depth through the preheater. The left and right-hand lines represent the low and high metal temperatures, respectively. The low temperature occurs as the element is first exposed to the flue gas after being cooled by the combustion air. The high temperature occurs just prior to exposure of the element to the combustion air.²

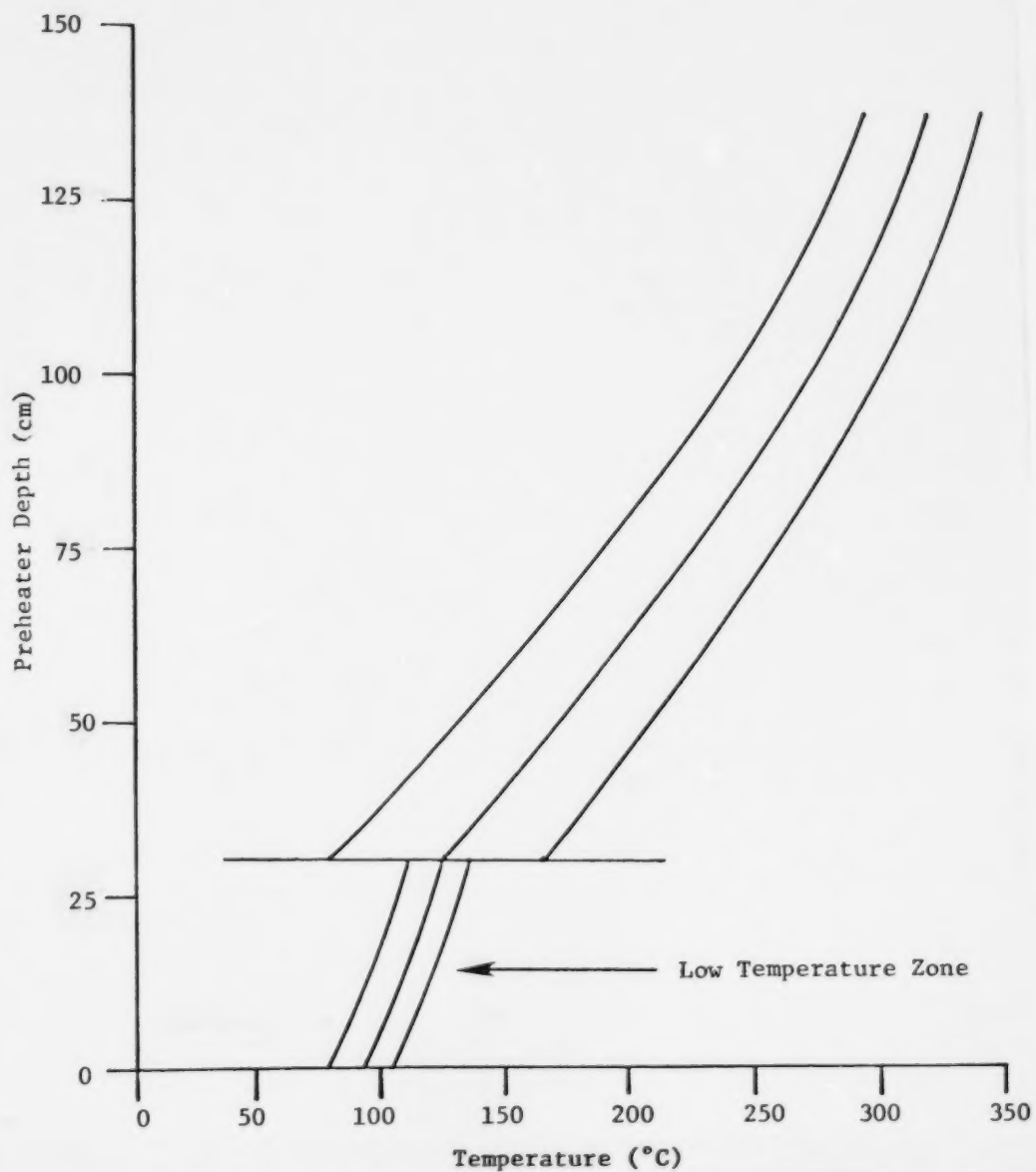


Figure 3-2. Temperature profile of heat transfer elements in a regenerative air preheater.

Examination of Figure 3-2 reveals some of the design features used to minimize air preheater plugging and corrosion by H_2SO_4 . As shown, the fluctuation of metal temperatures in the extreme cold end of the air preheater is less than the fluctuation in the higher temperature zones. This is due to the fact that the heat transfer elements in the cold end are made of a heavy-gauge, corrosion resistant metal having a different design or configuration when compared to the elements in the hot-end.

The cold-end heat transfer elements are constructed of heavy-gauge material designed to experience H_2SO_4 corrosion while maintaining structural strength. The increased element thickness in the cold-end allows the elements to corrode and still retain the strength to withstand the soot blower blast. In addition, the configuration of the elements is different consisting of spaced, flat sheets oriented parallel to the gas flow. This permits better penetration of the soot blower jet into the cold-end. The combination of heavy-gauge material and different element configuration tends to limit the temperature fluctuations in the cold-end as shown in Figure 3-2.

A typical regenerative air preheater design has provisions for removal and replacement of the cold-end elements once corrosion becomes serious (i.e., loss of metal or structural integrity). In many cases, the elements are rotated 180° after a specified period so that the corroded elements operate at higher temperatures and less corrosive conditions. The elements which are then exposed to severe acid condensation are essentially new. Using this technique, the service life of the cold-end elements can be increased.

Some other features of regenerative air preheaters which are used to minimize the impacts of H_2SO_4 condensation/plugging include soot blowers and water washing equipment. Soot blowing has been used as an effective technique for controlling and minimizing deposits. Soot blowers are usually located at the cold end of the air preheater on the gas outlet side. A high

pressure stream of either steam or air is directed onto the heat transfer elements. This dislodges the deposits which are then entrained by the flue gas and usually collected by downstream particulate removal equipment (e.g., an ESP).

Water washing is usually required to supplement soot blowing of the air preheater. Typically, washing is restricted to boiler outages. However, the frequency of water washing is ultimately determined by the pressure drop across the air preheater. Once the pressure drop increases beyond the level which can be tolerated by boiler ID fans, washing is required.

Depending on the number of preheaters it may or may not be necessary to operate at reduced load to permit isolation of a single preheater. When there are more than one preheater, it is usually possible to operate the boiler at more than a fraction of total load equivalent to the fractional number of air preheaters in service. For example, an installation with two air preheaters can operate at about two-thirds load with one preheater isolated and an installation with four preheaters could be expected to operate at full load with one preheater isolated.

In some cases the preheater can be washed while in operation. "On-stream" washing can only be applied in installations where the ductwork and location of drains will minimize the amount of moisture entering the dust collectors, precipitators, wind boxes, and boilers. Typically this requires that the air preheater be specifically designed to permit on-stream washing with the washing equipment installed on the air side of the preheater.⁶

3.2.2 Air Preheater Design and $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ Deposition

The design operating conditions for air preheaters are dictated by a number of factors. One of the most important is the temperature at which H_2SO_4 begins to condense (i.e., the acid dewpoint). If the flue gas is

cooled too much in the air preheater, H_2SO_4 can condense downstream of the preheater due to heat loss in ducts and the stack. This can cause corrosion of ductwork, fans, particulate collection equipment, etc. As a result, the temperature of the flue gas leaving the air preheater must be maintained far enough above the acid dewpoint to prevent downstream corrosion. This limits the cold-end metal temperature in an air preheater and thereby determines the maximum amount of heat which can be transferred from the flue gas to the air.

Deposition of ammonium salts can be controlled by maintaining the cold-end metal temperature above the formation temperatures of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$. However, the high formation temperatures of $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 (relative to the H_2SO_4 condensation temperature) would require a significant increase in the flue gas temperature at the air preheater exit. This would result in a significant decrease in the boiler thermal efficiency.

Figure 3-3 illustrates the relationship between $(\text{NH}_4)_2\text{SO}_4$, and NH_4HSO_4 formation temperatures and the air preheater temperature profile from Figure 3-2. The formation temperatures presented are for an SO_3 concentration of 10 ppm and for NH_3 concentrations ranging from 10 to 30 ppm. As shown, $(\text{NH}_4)_2\text{SO}_4$ can form in about 60 percent of the preheater while NH_4HSO_4 can form in 50 percent of the air preheater. It must be emphasized that the formation temperatures for $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 shown in Figure 3-3 are based on theoretical calculations. However, operating experience (Section 4) confirms that deposition occurs in both the intermediate and low temperature zones of the preheater.

The fact that $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposits can form in about 50 percent of an air preheater presents several problems. First, assuming a conventional air preheater design is employed, corrosion would occur in 50 percent of the heat transfer elements. To minimize this problem, corrosion resistant material would be required for approximately one-half the air preheater.

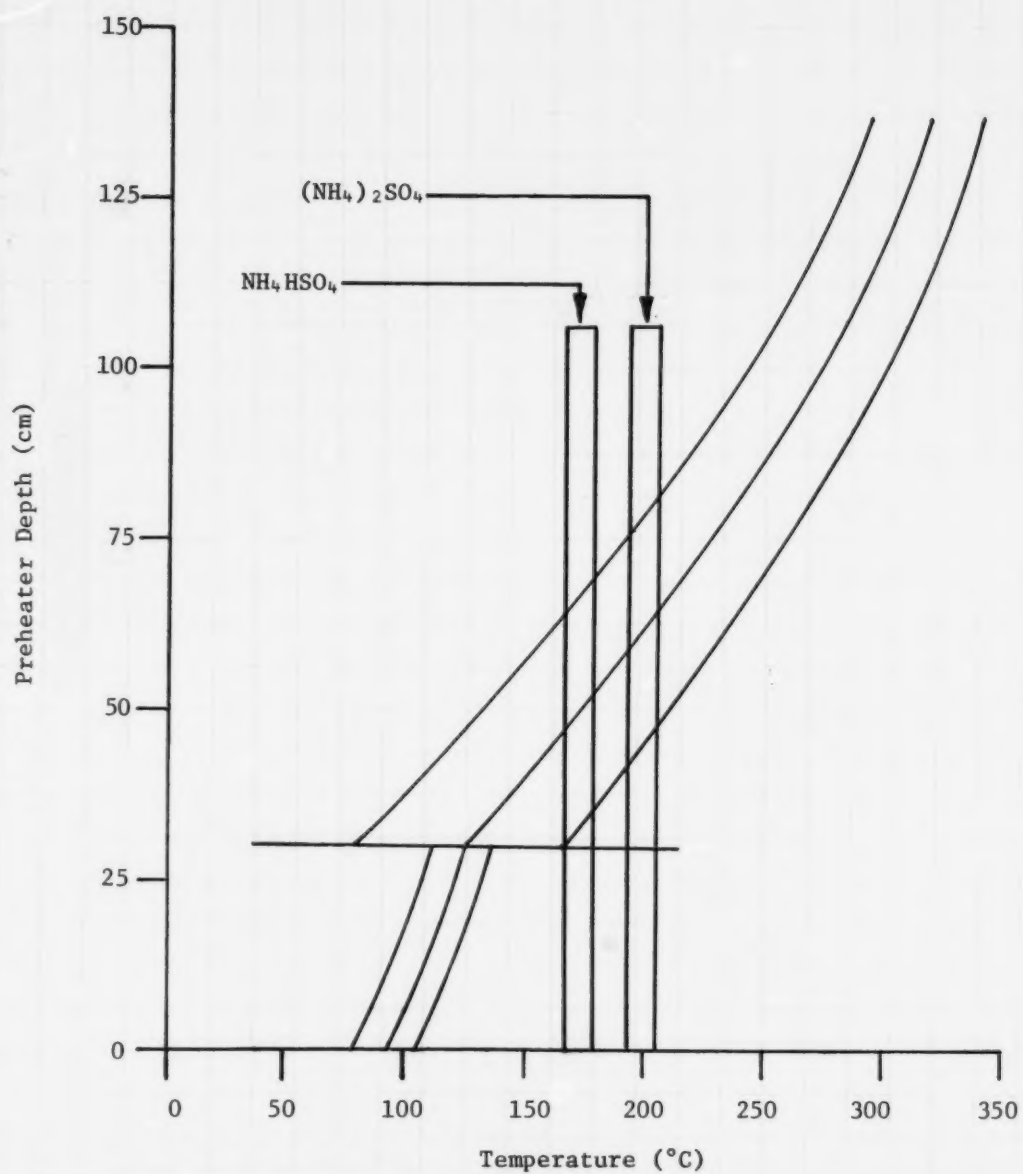


Figure 3-3. $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 formation temperatures in an air preheater.

Second, use of soot blowing equipment would not prove as effective in removing $\text{NH}_3\text{-SO}_3$ deposits as it is in removing H_2SO_4 deposits. This equipment must be located at the ends of the preheater while $\text{NH}_3\text{-SO}_3$ deposits can form in the center. The effectiveness of soot blowers could be improved by increasing the frequency and the operating pressure of the soot blowing medium (i.e., steam or air). However, this would tend to increase operating costs of the air preheater.

Finally, since soot blowing would not be as effective in controlling deposit formation, water washing may be required more frequently. This could require a special air preheater design to permit on-stream water washing. If a conventional design is employed, either forced boiler outages or periodic reductions in boiler load may be required to permit washing and thereby maintain acceptable air preheater performance.

Available data from SCR and SNR installations in Japan indicate that air preheater plugging problems do occur. In some cases, soot blowing is ineffective and more frequent water washing is required. However, the magnitude of the problem depends on the amount of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ that deposits in the air preheater which, in turn, depends on the concentrations of NH_3 and SO_3 in the flue gas.

One solution to the deposition problem is to raise the cold-end metal temperature above the formation temperature of $(\text{NH}_4)_2\text{SO}_4$ or NH_4HSO_4 . Based on Figure 3-3, it would be necessary to raise the flue gas temperature at the air preheater exit from 145°C to about 250°C to prevent formation of both $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 . In order to prevent NH_4HSO_4 formation, the temperature would have to be raised to approximately 230°C .

As mentioned previously, increasing flue gas temperature at the air preheater exit will decrease the thermal efficiency of the boiler. Figure 3-4 illustrates the approximate change in boiler efficiency as a function of the change in flue gas temperature at the air preheater exit.⁵ For the

"typical" preheater in Figure 3-3, increasing the exit temperature 105°C to 250°C (to prevent $(\text{NH}_4)_2\text{SO}_4$ formation) results in about a 5 percent decrease in efficiency. Increasing the exit temperature from 145°C to 230°C (to prevent NH_4HSO_4 formation) results in about a 4 percent decrease in efficiency.

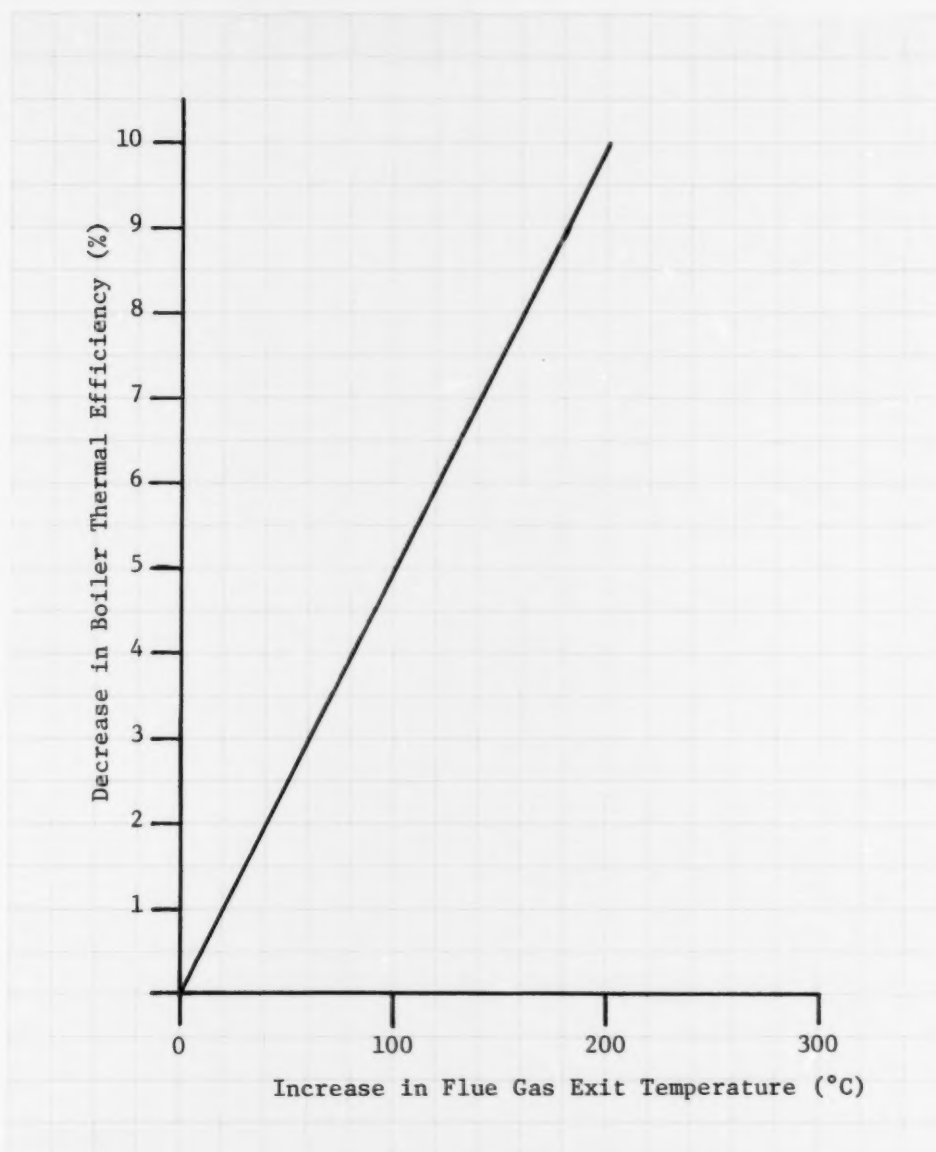


Figure 3-4. Change in boiler efficiency as a function of flue gas temperature at the air preheater exit.

3.3 CORROSION DUE TO NH_3 - SO_3 COMPOUNDS

A major problem associated with $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition in air preheaters is corrosion of the air preheater heat transfer elements. Ando and others have analyzed deposits found in air preheaters and identified NH_4 -Fe- SO_4 compounds which appear to be corrosion products. In addition, investigators in Japan have conducted laboratory tests which examined the corrosion of air preheater materials by NH_4HSO_4 and by mixtures of NH_4HSO_4 and other flue gas components.

This section presents a summary of available information on air preheater corrosion reactions and corrosion rates. In addition, the impact of corrosion on preheater operation is discussed. The information in this section was supplied by Dr. Ando as background for this study and includes work done by Dr. Ando and by other Japanese investigators.

3.3.1 Air Preheater Deposits

Dr. Jumpei Ando and K. Takemura collected and analyzed samples of deposits found in air preheaters. Each of the air preheaters was a Ljungstrom type located downstream of ammonia injection. The analyses conducted included X-ray diffraction to identify specific compounds and some chemical analyses to quantify deposit composition.³

In total, 11 samples were collected from 3 air preheaters. Table 3-2 identifies the installations where samples were collected and quantifies the gas compositions entering the air preheater. (A detailed discussion of each installation is presented in Section 4). Samples A-1 and A-2 were taken from deposits found in the low temperature zone of the preheater. Samples B-1 and B-2 were taken from the intermediate temperature zone and samples C-1 through C-7 were taken from deposits throughout the air preheater.

TABLE 3-2. AIR PREHEATER SAMPLES ANALYZED BY ANDO

Sample No.	Location	Boiler Fuel	Approximate Gas Composition (ppm)	
			SO ₃	NH ₃
A-1, A-2	Shindaikoywa Petrochemical's Yokkaichi Plant	High-Sulfur Oil	30-40	10
B-1, B-2	EPDC's Test Facility	Medium-Sulfur Coal	1-20	20-50
C-1 → C-7	Chubu Electric's Chita Plant	Low-Sulfur Oil	2-3	20-30

Table 3-3 presents the results of Ando's X-ray diffraction analyses of the air preheater deposits. As shown, the principal ammonium compounds found contained iron (Fe). These compounds are believed to be the result of reactions between NH_4HSO_4 and the air preheater elements.

The major component of deposits from location A was $\text{NH}_4\text{FeH}(\text{SO}_4)_2$, a possible corrosion product. In deposits from location B and C, the major components were fly ash and unburned carbon respectively. Other compounds from location B include $(\text{NH}_4)_3\text{Fe}(\text{SO}_4)_3$ which is also a possible corrosion product and $\text{NH}_4\text{Al}(\text{SO}_4)_2$, a possible product from reaction of fly ash and $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$. Deposits at location C contained both $\text{NH}_4\text{Fe}(\text{SO}_4)_2$ and $(\text{NH}_4)_3\text{Fe}(\text{SO}_4)_3$.

Examination of the deposit compositions in Table 3-3 reveals several facts. First, at locations B and C, it appears likely that $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposits acted as a site for accumulation of fly ash. This behavior is very similar to the manner in which H_2SO_4 condensation causes build-up of deposits in the cold end of an air preheater.

TABLE 3-3. ANALYSIS OF AIR PREHEATER DEPOSITS

Sample Number	Temperature Zone of Deposit Formation	Compounds and Relative Amounts Found		
		Major	Medium	Minor
A-1*	Low (cold)	$\text{NH}_4\text{FeH}(\text{SO}_4)_2$	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$	NH_4HSO_4
A-2	Low (intermediate)	$\text{NH}_4\text{FeH}(\text{SO}_4)_2$	-	$(\text{NH}_4)_3\text{Fe}(\text{SO}_4)_3$, $\text{NH}_4\text{Fe}(\text{SO}_4)_2$
B-1	Intermediate	Fly ash	$(\text{NH}_4)_3\text{Fe}(\text{SO}_4)_3$	$\text{NH}_4\text{Al}(\text{SO}_4)_2$, CaSO_4
B-2	Intermediate	Fly ash	$(\text{NH}_4)_3\text{Fe}(\text{SO}_4)_3$	$\text{NH}_4\text{Al}(\text{SO}_4)_2$, CaSO_4
C-1*	Low (cold)	Carbon	$(\text{NH}_4)_2\text{SO}_4$	-
C-2	Low (hot)	Carbon	$(\text{NH}_4)_2\text{SO}_4$	$(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$
C-3	Intermediate (cold)	Carbon	$(\text{NH}_4)_2\text{SO}_4$	$(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$
C-4	Intermediate (intermediate)	Carbon	$(\text{NH}_4)_3\text{Fe}(\text{SO}_4)_3$	$(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$
C-5	Intermediate (hot)	Carbon	$\text{NH}_4\text{Fe}(\text{SO}_4)_2$	$(\text{NH}_4)_3\text{Fe}(\text{SO}_4)_3$
C-6	High (cold)	Carbon	$\text{NH}_4\text{Fe}(\text{SO}_4)_2$	$(\text{NH}_4)_3\text{Fe}(\text{SO}_4)_3$
C-7	High (hot)	Carbon	$\text{NH}_4\text{Fe}(\text{SO}_4)_2$	-

*Note: The temperature zones A-1 + A-2 and C-1 + C-7 are listed in order of increasing temperatures. Sample C-1 was taken from the coldest part of the low temperature zone while Sample C-2 was taken from the hottest part of the low temperature zone, etc.

Another fact which is evident from the analyses is that $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposits reacted with iron from the steel heat transfer elements to form the $\text{NH}_4\text{-Fe-SO}_4$ compounds. These compounds are evidence of corrosion of the preheater material although the severity of the corrosion is uncertain and the mechanism by which the compounds form is not obvious.

3.3.2 $\text{NH}_4\text{HSO}_4\text{-Fe Reactions}$

Ando conducted laboratory experiments in an attempt to identify the reactions which occur between NH_4HSO_4 and iron. In addition, some tests were conducted using NH_4HSO_4 and fly ash. In these tests, powdered iron or fly ash was combined with NH_4HSO_4 in a porcelain crucible and subsequently heated. The duration of the tests ranged from 30 to 120 minutes. At the end of each test, the contents of the crucible were removed and analyzed by X-ray diffraction.

Table 3-4 presents the results of Ando's laboratory experiments with iron and NH_4HSO_4 . As shown, the relative amounts of each compound change as a function of time and temperature. At temperatures below 200°C , the analysis at 30 minutes identified NH_4HSO_4 as the major compound. The amount of NH_4HSO_4 decreased with time while the concentrations of $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ (a double salt mixture of $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4) and $\text{NH}_4\text{FeH}(\text{SO}_4)_2$ increased. At temperatures above 200°C , almost no NH_4HSO_4 was present after 30 minutes and the principal products were $(\text{NH}_4)_3\text{Fe}(\text{SO}_4)_3$ and $\text{NH}_4\text{Fe}(\text{SO}_4)_2$. Ando reported that the reaction products also contained unreacted iron and that large amounts of NH_3 and SO_3 were vaporized during the experiments.

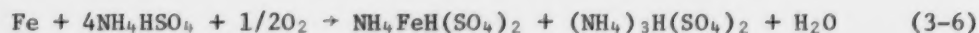
A comparison of Tables 3-3 and 3-4 indicates that all the $\text{NH}_4\text{-Fe-SO}_4$ compounds which were present in air preheater deposits analyzed by Ando could be produced by reaction of NH_4HSO_4 and Fe in the laboratory. In addition, the experimental temperature dependence of the reaction products corresponds well with the temperature zone in the air preheater where specific

TABLE 3-4. $\text{NH}_4\text{-Fe-SO}_4$ COMPOUNDS PRODUCED BY ANDO IN LABORATORY TESTS

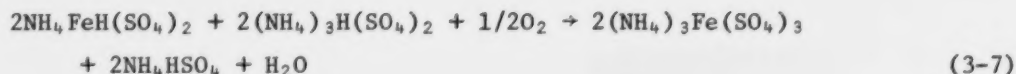
Temperature (°C)	Time (Minutes)	Compounds Formed and Relative Amounts				
		NH_4HSO_4	$(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$	$\text{NH}_4\text{FeH}(\text{SO}_4)_2$	$(\text{NH}_4)_3\text{Fe}(\text{SO}_4)_2$	$\text{NH}_4\text{Fe}(\text{SO}_4)_2$
150	30	Major	Minor	Minor	-	-
150	60	Major	Medium	Medium	-	-
150	120	Medium	Major	Major	-	-
200	30	Major	Medium	Medium	-	-
200	60	Medium	Medium	Minor	Minor	-
200	120	Minor	Medium	Minor	Major	-
250	30	-	-	-	Major	-
250	60	Minor	-	-	Medium	Minor
250	120	Minor	-	-	Medium	Medium
300	30	Minor	-	-	Minor	Major
300	60	-	-	-	-	Major
300	120	-	-	-	-	Major

products were found. One product which was not found in the laboratory tests was $\text{FeSO}_4 \cdot \text{H}_2\text{O}$. This is probably a product of the reaction of H_2SO_4 and Fe.

Ando has identified possible reactions which account for the products found in both laboratory experiments and in actual deposit samples. At 150 to 200°C, NH_4HSO_4 and Fe can react as illustrated by Equation 3-6.



As the temperature increases above 200°C, the reaction illustrated by Equation 3-7 occurs:

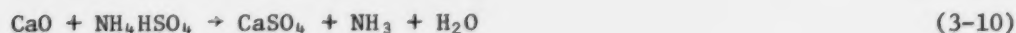
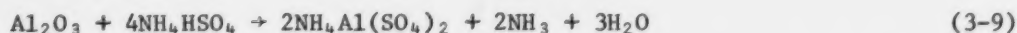


And finally, at 250 to 300°C, the reaction represented by Equation 3-8 can occur.



It should be noted that Equations 3-6, 3-7, and 3-8 illustrate overall reactions and probably do not represent actual reaction mechanisms.

Ando also conducted tests with NH_4HSO_4 and fly ash which contained SiO_2 (56 percent), Al_2O_3 (26 percent), and CaO (5 percent). Reaction products found after heating include $\text{NH}_4\text{Al}(\text{SO}_4)_2$ and CaSO_4 . Overall reactions which account for these products are illustrated by Equations 3-9 and 3-10 respectively.



These products correspond to compounds found in the deposits at location B which contained large quantities of fly ash.

3.3.3 Laboratory Corrosion Studies

A series of laboratory tests were conducted by investigators in Japan to determine the corrosivity of liquid NH_4HSO_4 . Corrosion rates were measured for 4 types of steel as a function of time, temperature, and the ratio of the volume of NH_4HSO_4 to the surface area of the steel specimen. In addition, tests were conducted which determined the impact on the corrosion rate of individually adding H_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, CaO , KCl , MgO , or Fe_2O_3 to the NH_4HSO_4 .

The 4 types of steel tested include mild steel, low alloy steel, and 304 and 316 stainless. The chemical compositions are presented in Table 3-5. Specimens of each steel were weighed before and after being placed in molten NH_4HSO_4 and thus the corrosion rate was determined.

Figure 3-5 presents a comparison of the amount of corrosion experienced by the 4 types of steel tested. Temperature was maintained at 200°C and 50 grams of NH_4HSO_4 were used. As shown, the low alloy steel exhibited the greatest amount of corrosion followed by the mild steel. Both the 304 and 316 stainless steels showed a relatively low amount of corrosion. The corrosion rates of the low alloy and mild steel (equal to the slope of the corrosion vs. time curves in Figure 3-5) are nearly equal. In addition, the corrosion rates of the 304 and 316 stainless are equal but much lower than the corrosion rates for low alloy and mild steel.

An interesting aspect of Figure 3-5 is that the amount of corrosion experienced by both the low alloy and the mild steel continues to increase with time. On the other hand, the two types of stainless experienced relatively rapid corrosion initially but after about 20 to 30 hours, very little additional corrosion was observed. This could have significant implications

TABLE 3-5. CHEMICAL COMPOSITION OF STEEL ALLOYS TESTED

Alloy	Amount of component (wt %)									
	C	Si	Mn	P	S	Cr	Ni	Cu	Mo	
SS41 - Mild steel	-	-	-	<0.05	<0.05	-	-	-	-	
Low alloy steel	0.07	0.27	0.36	0.075	0.017	0.36	0.10	0.28	-	
304 stainless	0.05	0.60	0.92	0.026	0.005	18.32	0.15	-	-	
316 stainless	0.06	0.59	1.06	0.031	0.004	16.90	12.50	0.29	2.79	

in terms of air preheater design. Air preheater materials are typically mild steel, which, according to these laboratory tests will experience corrosion at a relatively high rate. It may, therefore, be necessary to employ stainless steel in air preheaters designed for service downstream of an SCR system. Another alternative, not examined in these tests but which has been used successfully in oil-fired applications to control H_2SO_4 corrosion, is glass enameled steel. This seems to be the material of choice in Japan where available data indicate it is relatively immune to corrosion by $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposits.

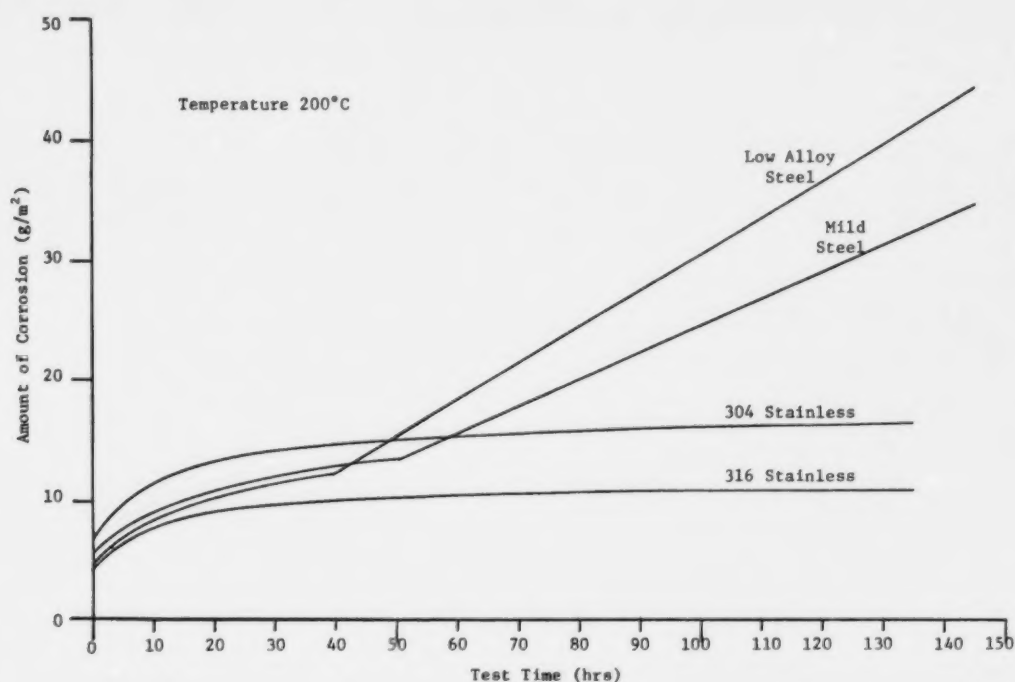


Figure 3-5. Amount of corrosion for various steel alloys by liquid NH_4HSO_4 .

Figure 3-6 presents the corrosion rate of low-alloy and mild steel as a function of temperature. As shown, the corrosion rate is reduced by a factor of ten as the temperature is reduced from 230 to 170°C. In terms of air preheater operation, this indicates that the most serious corrosion would be expected to occur at the point where NH_4HSO_4 begins to form. Corrosion would be less serious in cooler parts of the preheater.

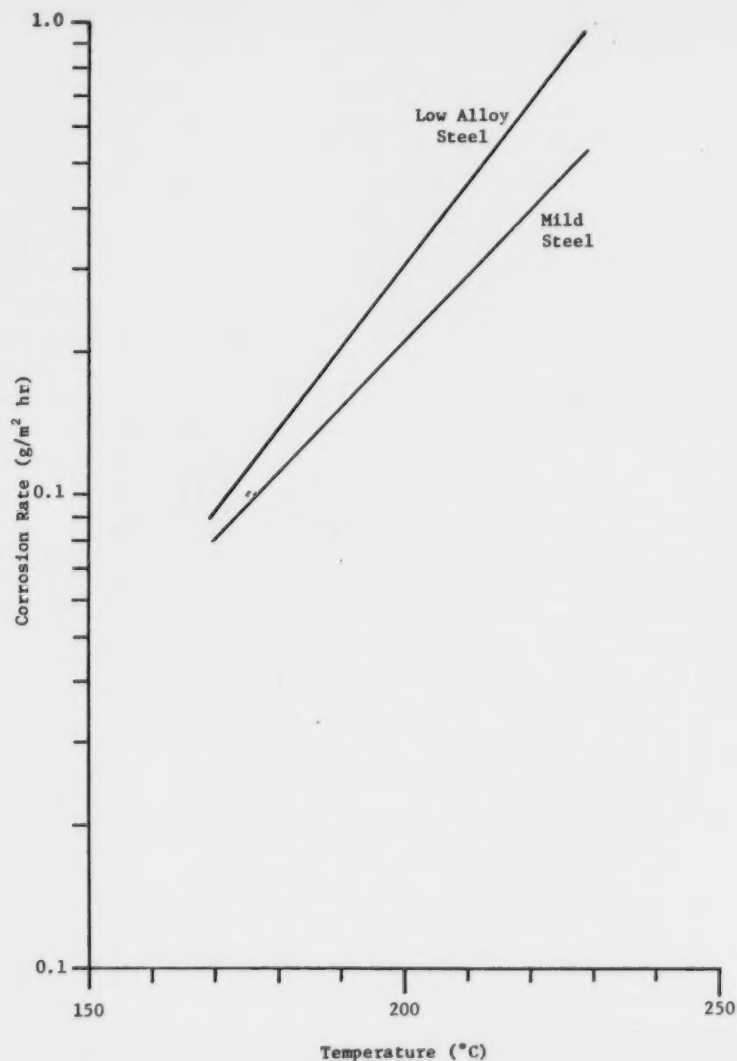


Figure 3-6. Corrosion rate as a function of temperature.

Figure 3-7 compares the corrosivity of NH_4HSO_4 with a mixture of 92.6 weight percent NH_4HSO_4 and 7.4 weight percent H_2SO_4 . As shown, the initial corrosion rate of the mixture is about 100 times greater than the corrosion rate of pure NH_4HSO_4 . However, after about 100 hours, the corrosion rate of the mixture is reduced and is nearly equal to that of the pure NH_4HSO_4 . This behavior is probably due to the neutralization of the H_2SO_4 by reaction with iron.

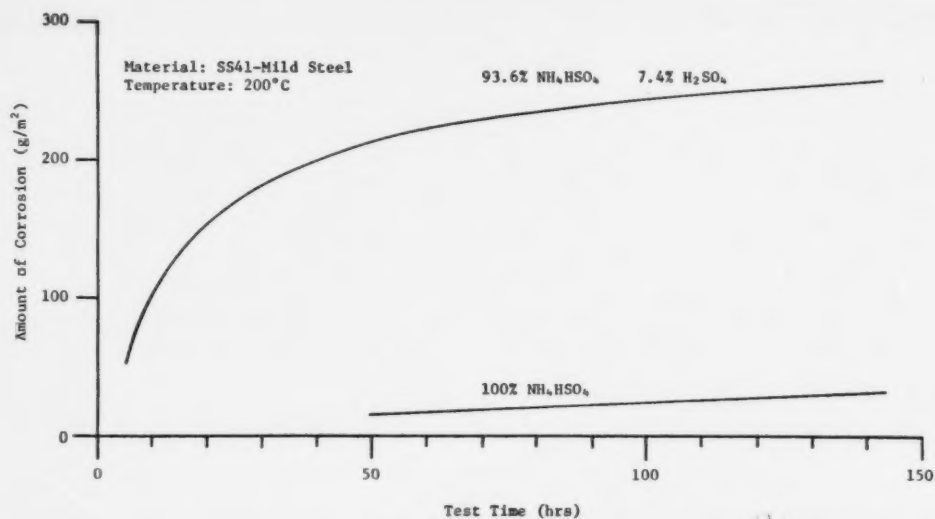


Figure 3-7. Corrosivity of pure NH_4HSO_4 vs. NH_4HSO_4 - H_2SO_4 mixture.

Figure 3-8 shows the impact of adding $(\text{NH}_4)_2\text{SO}_4$ to the molten NH_4HSO_4 . As illustrated, even a small quantity of $(\text{NH}_4)_2\text{SO}_4$ can reduce the amount of corrosion by 50 percent or more. In terms of preheater operation, this effect could tend to offset the adverse impact of high temperatures since $(\text{NH}_4)_2\text{SO}_4$ is more likely to form at higher temperatures.

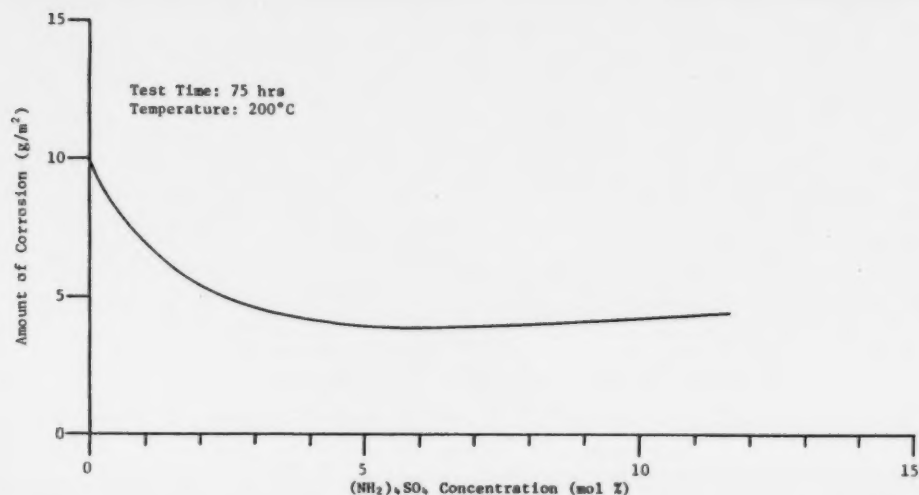
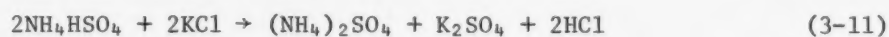


Figure 3-8. Effect of $(\text{NH}_4)_2\text{SO}_4$ on corrosion of mild steel.

The effects of some other additives on the NH_4HSO_4 corrosion rate are presented in Table 3-6. Calcium, magnesium, and iron oxides all tend to reduce the corrosion rate by neutralizing some of the NH_4HSO_4 . The aluminum and silicon oxides do not appear to have a significant effect while KCl , NH_4Cl , and $\text{Fe}_2(\text{SO}_4)_3$ all increase the corrosion rate significantly. The Japanese investigators reported that addition of KCl and NH_4Cl resulted in the formation of HCl which caused the increased corrosion (Equations 3-11 and 3-12).



The effect of $\text{Fe}_2(\text{SO}_4)_3$ may be due to a similar reaction which produces H_2SO_4 (Equation 3-13).

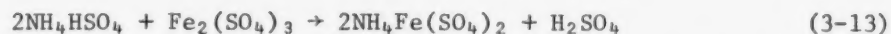


TABLE 3-6. EFFECT OF NH_4HSO_4 - ADDITIVE MIXTURES ON CORROSION OF LOW-ALLOY STEEL

Additive	Additive Concentration (wt %)	Amount of Corrosion (g/m^2)	Corrosion Rate ($\text{g}/\text{m}^2 \text{ hr}$)
None	-	22.5	0.30
CaO	18.3	13.7	0.19
MgO	20.0	7.0	0.09
Al_2O_3	16.7	22.1	0.30
Fe_2O_3	20.6	12.4	0.17
SiO_2	37.5	27.2	0.37
KCl	25.9	261.2	3.47
NH_4Cl	27.5	114.8	1.53
$\text{Fe}_2(\text{SO}_4)_3$	27.0	383.2	5.11

3.4 IMPACT OF DEPOSIT FORMATION ON AIR PREHEATER PERFORMANCE, OPERATION AND MAINTENANCE

The deposition of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ in an air preheater can impact the preheater's performance, operation and maintenance. Sections 3.1 through 3.3 have identified fundamental aspects of the deposition problem, primarily plugging and corrosion of the air preheater. This section presents a discussion of how air preheater performance, operation, and maintenance may be affected by formation and deposition of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$. The basis for this discussion is the assumption that a conventional, regenerative air preheater design is employed. Where appropriate, possible design modifications which minimize the adverse impact of deposition are discussed.

3.4.1 Air Preheater Performance and Operation

There are two aspects of air preheater performance which must be considered; thermal efficiency and pressure drop through the preheater. The most important aspect is the thermal efficiency which is a measure of the heat that is transferred from the flue gas to the combustion air. The thermal efficiency is a complex function of gas and air flow rates, heat transfer coefficients, heat capacities, and several design parameters (e.g., weight of the heat transfer elements) of the air preheater.⁷ Thermal efficiency is significant since a decline in efficiency, as evidenced by an increase in flue gas temperature at the air preheater exit, will decrease the efficiency of the boiler (Figure 3-5).

The impact of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition on the thermal efficiency of the air preheater is not expected to be significant. The results of tests conducted by the Electric Power Development Company (EPDC) in Japan showed no evidence of a decline in the thermal efficiency of the preheater due to deposition of ammonium sulfates.⁸ In addition, another study reported that the presence of soot and fly ash deposits can actually improve the thermal efficiency of the air preheater. This is a result of the deposits increasing the heat capacity of the air preheater.⁷ However, this would not be true in the case of recuperative

air preheaters where deposits tend to impair preheater efficiency by increasing the overall resistance to heat transfer.

Pressure drop through the air preheater is also an important aspect of preheater performance. An increase in pressure drop through the preheater can cause a slight decline in the thermal efficiency of the boiler as shown in Figure 3-9. Increased pressure drop can present an additional problem. If the increase is too large, the existing fans may not be capable of maintaining full load flow rates and the boilers would have to be derated.

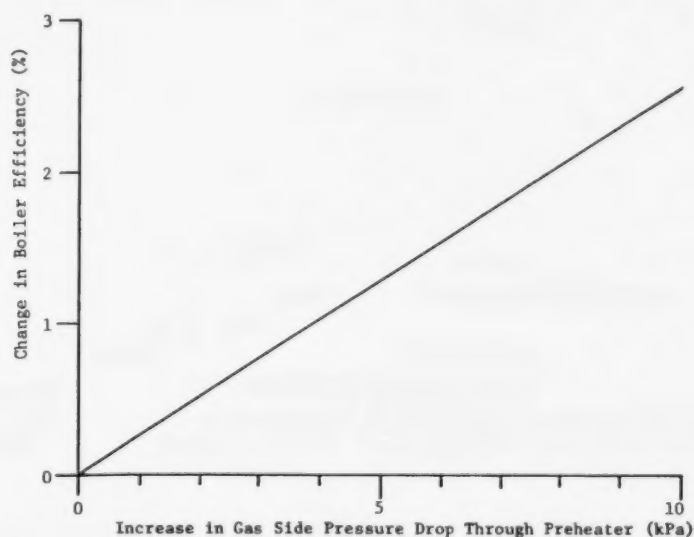


Figure 3-9. Change in boiler efficiency as a function of pressure drop through the air preheater.

$(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition can have an adverse impact on the pressure drop through the preheater. Experience in Japan indicates that the air preheater pressure drop can increase despite the use of soot blowing. This necessitates an increase in water washing of the preheater. The most serious

case reported by Ando required a forced boiler outage to permit waterwashing about every three months. In other cases, no waterwashing was necessary. The extent of the problem and the required washing frequency depends on the quantity of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ which deposits.

3.4.2 Air Preheater Maintenance

Deposition of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ in an air preheater will increase the maintenance requirements of the unit. This may include an increase in the pressure of the soot blowing medium and the frequency of soot blowing. In addition, the required frequency of water washing can increase while evidence indicates that the service life of the heat transfer elements may decrease due to corrosion.

A number of variables determine the soot blowing requirements for a given installation. Some of the more important variables include the size of the preheater, the type of fuel fired, and the operating temperatures of the preheater. Typically, the soot blowing cycle is initiated once every eight hours and the pressure of the soot blowing medium ranges from 1.48 to 1.82 MPa (200 to 250 psig) for steam and 1.34 to 1.48 MPa (180 to 200 psig) for compressed air. In practice, the soot blowing frequency is determined by the pressure drop across the preheater. Once the pressure drop reaches a specified level, the soot blowing cycle is initiated. The operating pressure of the soot blowing medium is limited by the strength of the heat transfer elements.

At installations where NH_3 is present in the flue gas and deposition occurs, both the soot blowing frequency and the soot blowing pressure would be greater than the soot blowing requirements in comparable installations where no NH_3 is present. Unfortunately, no operating data are available which quantify the relationship between $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposit formation and soot blowing requirements. Information supplied by Ando does indicate

that in several SCR/SNR applications, use of existing soot blowing equipment is not very effective in controlling preheater deposits. For more effective cleaning, additional equipment can be installed to provide both hot- and cold-end soot blowing (most air preheaters only have cold-end soot blowers).⁶ Also, the operating pressure of the soot blowing medium could be increased to the maximum compatible with the heat transfer element strength and the soot blowing equipment.

Air preheater water washing frequency will also be impacted by $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition. Typically, the air preheater is only washed during boiler outages although the washing frequency is dependent on the rate at which deposits (and pressure drop) increase. Experience at installations in Japan indicates that water washing is a very effective method of removing $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposits although the washing frequency may increase due to the presence of deposits. As previously discussed, in-service water washing equipment should be considered for inclusion in the design of an air preheater located downstream of an SCR system.

Corrosion of heat transfer elements in the preheater may also result from deposition of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$. This can cause a decrease in the service life of elements in the intermediate temperature zone of the air preheater where deposits begin to form (Section 3.2). However, the presence of NH_3 may also serve to retard corrosion in the extreme cold end of the air preheater by reducing the potential for H_2SO_4 condensation. In fact, there are several cases reported where NH_3 injection has been used to successfully control corrosion in the preheater.⁹ This would also have a beneficial effect on potential for acid corrosion in downstream ductwork and equipment. The neutralization of H_2SO_4 by NH_3 can serve to improve or extend the service life of downstream equipment. Additionally, it may be possible to reduce material costs for the downstream equipment.

Unfortunately, the results of corrosion studies conducted with liquid NH_4HSO_4 cannot be used to predict the service life of preheater materials. The laboratory test conditions do not directly simulate the conditions in a preheater. However, the results of these tests do identify the relative corrosion experienced by several materials. The tests also indicate that corrosion due to NH_4HSO_4 is much lower than corrosion due to H_2SO_4 .

Information available from EPDC's test facility indicates that the service life of intermediate temperature zone elements is in the range of 5 to 10 years.⁸ Based on these tests results and the location of deposit formation in a typical preheater, it appears that some type of corrosion resistant material would be needed in the intermediate temperature zone. This could be a heavy-gauge, mild steel similar to the type used in the extreme cold-end of the preheater or it may be necessary to use a material such as 304 stainless or glass enameled steel. The choice is obviously an economic one and will depend on the difficulty, and thus the cost, of replacing heat transfer elements in the intermediate temperature zone versus the increased cost of corrosion resistant materials.

3.5 ENVIRONMENTAL IMPACT OF $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ DEPOSITION IN AIR PREHEATERS

Ammonia emitted from SCR and SNR systems can affect operation of downstream equipment and may also have some environmental impacts. The scope of this study was limited to the effects of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition in air preheaters and so no consideration is given to impacts downstream of the preheater. The major operational impacts of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ have been discussed in Section 3.1 through 3.4. This section discusses the environmental impact of deposit formation in air preheaters.

The only environmental impact which is expected to result from deposition of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ will be associated with the water stream which is used to wash deposits from the preheater. This stream can contain dissolved NH_4 , SO_4 , Fe, and other compounds which may be present in fly ash. The actual composition of the wash water will be similar to the composition of water from conventional air preheater washing. The principal difference is the presence of NH_4 and possibly higher Fe concentrations than normal.

Air preheater wash water is classified as a metal cleaning waste and as such, it must meet the discharge limits which are shown in Table 3-7.¹⁰ This waste stream can be treated separately or it may be combined with other metal cleaning wastes in a single treatment facility. The type of treatment employed is site specific. In some cases, the metal cleaning waste can be routed to existing ash basins where the copper and iron will precipitate in the form of insoluble hydroxides. In other installations, wastes are treated by raising the pH with lime or some other suitable alkali. This also results in precipitation of metal hydroxides.¹¹

TABLE 3-7. DISCHARGE LIMITS FOR METAL CLEANING WASTES

Stream Pollutant	Emission Limit for New Sources (mg/l)	
	Maximum	Average
Total Suspended Solids	100	30
Oil and Grease	20	15
Copper (total)	1	1
Iron (total)	1	1

Typically, metal cleaning wastes contain copper and iron, as shown in Table 3-8 and, depending on the cleaning process used, significant amounts of NH_3 may be present. Some typical boiler cleaning chemicals include ammoniated citric acid, ammoniated EDTA, and ammonical sodium bromate. Use of these chemicals can result in NH_3 concentrations ranging from 700 to 5200 mg/l in the waste stream.¹²

TABLE 3-8. METAL CLEANING WASTE CHARACTERISTICS

	Boiler Cleaning	Boiler Cleaning	Air Preheater Cleaning
Suspended Solids, mg/l	5-74	595-6465	820-220
Iron, mg/l	34-1645	150	3-1700
Copper, mg/l	13-131	1	0-5

NH_3 can impact the treatment of metal cleaning wastes since it can form complexes with copper ions. Formation of a Cu-NH_3 complex increases solubility of Cu and thereby limits the effectiveness of alkaline precipitation treatment. However, experimental data indicate that the Cu-NH_3 complex¹¹ dissociates when the NH_3 concentration is below 0.1 molar (17,000 mg/l).

Currently there are no discharge limits for NH_3 in metal cleaning wastes (Table 3-7) although EPA has proposed to add NH_3 to the priority pollutant list. If this occurs, discharge limits would be required for NH_3 and some form of treatment might be necessary for metal cleaning wastes and consequently for air preheater wash water containing NH_3 . At this time, however, it appears unlikely that NH_3 will actually be added to the priority pollutant list.¹³ In any event, it appears that the environmental impact of air preheater wash water containing NH_3 will be minimal.

Analysis of wash water from an air preheater located downstream of an SCR system indicated an average NH_3 concentration of 8 mg/l. As a maximum, the NH_3 concentrations of preheater wash water should be less than 100 mg/l. These concentrations are less than those expected in typical metal cleaning wastes and well below the levels which can adversely impact the waste treatment process. As a result, the most significant impact of NH_3 in the air preheater wash water will be to increase the volume of air preheater wash water which must be treated. In some power plants, this treatment is conducted on a contract basis and thus, an increase in the quantity of waste will increase the treatment requirements. Therefore, the only impact of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition may be to increase the cost of treating air preheater wash water.

SECTION 4

EXPERIENCE WITH AIR PREHEATER PLUGGING/CORROSION DUE TO DEPOSITION OF $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$

Reports from Japan have indicated that corrosion and plugging of air preheaters located downstream of selective catalytic reduction systems represent one of the principal problems associated with application of this technology.^{1,2} This section presents a summary of available information on air preheater plugging and corrosion. Most of the data presented here represent Japanese experience. Some additional information is presented which represents the results of experience with conditioning fly ash by injection of ammonia into the flue gas and with the use of ammonia to reduce acid condensation and corrosion in air preheaters.

The discussion presented here will focus on three areas:

- where and under what conditions do deposits form in the air preheater and what are the compositions of these deposits
- how serious are the corrosion problems which result from deposition of these compounds
- what procedures are employed to limit deposits or are required to maintain acceptable operation of the air preheater

The information concerning the Japanese experience in these areas is more extensive than the reports of experience not associated with NO_x removal systems. This section contains a summary of both the Japanese and other data which relate to $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition in air preheaters.

4.1 JAPANESE EXPERIENCE WITH AIR PREHEATER PLUGGING CORROSION AND MAINTENANCE

Over 60 SCR and SNR systems are operating in Japan.¹ Most of these systems treat gas streams which contain little or no SO_2/SO_3 . As a consequence, no problems with $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition would be expected. However, some of the SCR and SNR systems treat flue gas from combustion of high-sulfur oil and from iron ore sintering processes which do have SO_2/SO_3 present. This section summarizes the operating experience at selected SCR and SNR systems in Japan. In addition, details of a test facility operated by the Electric Power Development Company (EPDC) of Tokyo, Japan are presented.

As background for this study, Dr. Jumpei Ando conducted a survey of nine SCR and SNR systems in Japan. In addition, a recent survey of Japanese SCR technology sponsored by the EPA documented operating experience at three SCR installations. The magnitude of the air preheater problems at these installations ranged from no observable deposits to severe plugging and corrosion of the air preheaters. Data were obtained which, in most cases, quantify the concentrations of NH_3 and SO_3 in the flue gas and identify the type and operating conditions of the air preheater.

Table 4-1 presents a summary of the survey conducted by Ando and the EPA and also includes data from EPDC's test facility. As shown, the installations surveyed comprise a variety of processes (both the NO_x reduction system and the process being controlled) and sizes. Unfortunately, the data on NH_3 and SO_3 concentrations at the air preheater inlet are not complete.

The relative severity of deposit formation for each installation was determined based on reports of operating experience. The primary factor considered was the rate at which the air preheater plugged. It should be noted that the severities presented in Table 4-1 are somewhat subjective.

TABLE 4-1. SUMMARY OF EXPERIENCE AT SELECTED SCR AND SNR INSTALLATIONS IN JAPAN

Plant	Application	Process/ Vendor	Size		Air Preheater Type	Flue Gas Temperature (°C)		NH ₃ at A.P. Inlet (ppm)	SO ₂ at A.P. Inlet (ppm)	H ₂ O at A.P. Inlet (%)	Relative Severity of Deposit Formation
			Nm ³ /hr	scfm		A.P. Inlet	A.F. Outlet				
Shindaiyowa Petrochemical, Yokkaichi Plant	Steam Generator 3% Sulfur Oil	SCR/ Hitachi Zosen	440,000	274,000	Ljungstrom	410	163	10	30-40	16	Severe
Kurabo, Hirakata Plant	Steam Generator High Sulfur Oil	SCR/ Kurabo	30,000	18,700	Tubular	400	220	3-10	40	-	Minor
Nippon Yakin, Kawasaki Plant	Steam Generator High Sulfur Oil	SCR/ Mitsubishi Kakoki	15,000	9,300	Rothemuehle	385	270-300	10-20	20-30	-	None
Chubu Electric, Chita Station	Steam Generator 0.2% Sulfur Oil	SNR/ MHI/Exxon	1,050,000	653,000	Ljungstrom	-	-	20-30	2-3	-	Moderate
Mitsui Petrochemical, Chiba Plant	Steam Generator	SNR/Ionon Technology	120,000	75,000	Ljungstrom	-	-	10-20	-	-	None
Mitsui Petrochemical, Chiba Plant	Steam Generator 0.2% Sulfur Oil	SCR/Mitsui Engineering	200,000	124,000	-	-	-	5	5*	-	None
EPDC, Takasago Plant	Steam Generator 2% Sulfur Coal Slipstream	NH ₃ Injec- tion for test pur- poses only	9,000	5,600	Ljungstrom	280-300	130-150	20,50	1-20	-	Moderate- Severe
Kawasaki Steel, Chiba Plant	Iron Ore Sintering	SCR/ Hitachi Zosen	850,000	529,000	Ljungstrom	400	160-180	10	2	-	Minor
Nippon Steel, Kimitsu Plant	Iron Ore Sintering	SCR/ JGC Corp.	2,000	1,250	Rothemuehle	285	175	20-50**	5-15	-	Severe
Nakayama Steel, Funasachi Plant	Iron Ore Sintering	SCR/ Nigata Engineering	6,000	3,700	Ljungstrom	280-350	180-220	5	10-20	7-10%	Minor
Chugoku Electric Kudamatsu Station	Steam Generator 0.2% Sulfur Oil	SCR/ IHI	1,290,000	804,000	-	-	140	4	4	-	Severe
Chugoku Electric Shimonoseki Station	Steam Generator Low Sulfur Coal/ Medium Sulfur Oil	SCR/ MHI	550,000	342,000	Ljungstrom	-	160	0.5	-	-	None
Fuji Oil Sodegaura Refinery	Steam Generator 0.4% Sulfur Oil	SCR/ MHI	280,000	175,000	Tubular Economizer	330-370	180	-	-	-	Minor- Moderate

*Estimated based on flue gas SO₂ concentration**Estimated based on NH₃/NO_x mole ratio at reactor inlet

A qualitative examination of the data reveals some general trends. Most systems which operate with well controlled NH_3 emissions (less than 10 ppm NH_3 at the preheater inlet) do not appear to have a severe problem with plugging and/or corrosion. The data also indicate that at installations with NH_3 concentrations above 10 ppm, the severity of the air preheater plugging increases as the SO_3 concentrations increase. These trends appear to be consistent with the results of Radian's thermodynamic and kinetic analyses of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ formation. A detailed discussion and analysis of the data presented in Table 4-1 is included in Section 5.3.

Although Table 4-1 summarizes pertinent data, some of the specific details of each installation are also of interest. In an effort to provide more detailed background on the problems, a brief summary of the experience at each plant will be presented. The following discussion highlights the salient points of the surveys conducted by Dr. Ando and the EPA and also describes some of the results from EPDC's test facility.

4.1.1 Experience at Shindaikyowa Petrochemical's Yokkaichi Plant

Plant Description

This plant has a Hitachi Zosen SCR system for NO_x control in conjunction with a Wellman Lord-MKK sodium scrubbing system for SO_2 removal. The pollution control equipment is installed on a 140 MW equivalent steam generator firing 3 percent sulfur oil. Flue gas from the boiler contains about 1500 ppm SO_x and 150 ppm NO_x .

Figure 4-1 presents a schematic of the scrubber-air preheater-SCR system at the Yokkaichi plant. Gas is first treated by the flue gas desulfurization (FGD) system where approximately 90 percent of the SO_2 and most of the particulates are removed. This gas stream enters the low temperature side of a Ljungstrom air preheater, passes through a supplementary oil fired heater

and enters the catalytic reactor. Ammonia is injected just upstream of the reactor at a rate of 0.9 moles per mole NO_x which results in nearly a 90 percent reduction in NO_x emissions. The flue gas leaves the reactor and enters the high temperature side of the Ljungstrom preheater where it is cooled from 410 to 163°C. At the inlet to the air preheater, the gas contains approximately 30-40 ppm SO_3 and 10 ppm NH_3 .

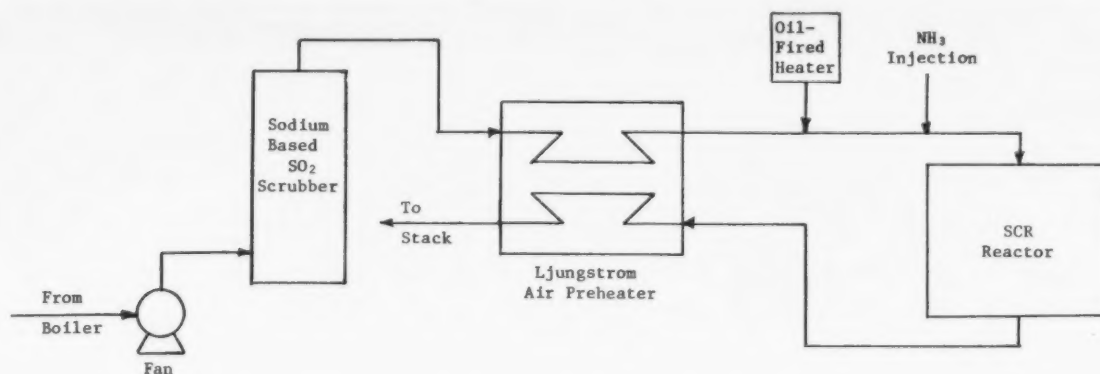


Figure 4-1. Pollution control system at Shindaikyowa Petrochemical's Yokkaichi Plant.

Operating Experience

The plant started up in December, 1975. During the first two months of operation there was no appreciable increase in pressure drop through the air preheater. Then in a period of about four weeks, the pressure drop across the air preheater increased until it reached a safety limit (over twice the initial pressure drop) and the plant was shut down. Upon inspection, solid deposits were found in the low-temperature zone and to a lesser extent in the intermediate temperature zone of the air preheater. The deposits were removed from the air preheater passages by washing with approximately 136 m³ (36,000 gal) of water.

Cleaning of the air preheater required approximately two days, after which operation of the plant was resumed. Approximately 3 months later, the pressure drop through the air preheater again reached the safety limit and the plant was shut down. The rate at which the pressure drop increased was similar to the first experience (i.e., a rapid increase toward the end of the three month period). The air preheater was washed again and after two days, operation was resumed.

During the initial 15 months of operation at the plant, water washing of the air preheater has been required a total of 5 times. Use of existing sootblowing equipment has not been effective in reducing the rate at which the air preheater plugging occurs. Since March, 1977, efforts have been made to reduce the quantity of deposits and the rate at which the air preheater plugs. A stronger sootblowing system was installed and the NH_3 injection ratio was lowered but these actions have only had limited success.

Corrosion of the Air Preheater

After 4,740 hours of operation, the Ljungstrom air preheater was examined for evidence of corrosion. Corrosion was observed at the following locations in the low-temperature zone of the air preheater:

- the radial seal
- the edge of the enamel-coated heat transfer material
- the expansion cover

Unfortunately there are no data which quantify the extent of this corrosion although Ando's survey classifies it as "serious".

Analyses of deposits found in the low and intermediate temperature zones are shown in Table 4-2. Based on this analysis, it appears that the

initial deposits consisted of NH_4HSO_4 and H_2SO_4 . These compounds then reacted with iron in the air preheater to form the compounds shown in Table 4-2.

TABLE 4-2. ANALYSES OF DEPOSITS FOUND IN THE AIR PREHEATER AT SHINDAIKYOWA PETROCHEMICAL'S YOKKAICHI PLANT

Deposit Location	Relative Amount of Compounds Found		
	Major	Medium	Minor
Low Temperature Zone (cold end)	$\text{NH}_4\text{FeH}(\text{SO}_4)_2$	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$	NH_4HSO_4
Low Temperature Zone (intermediate)	$\text{NH}_4\text{FeH}(\text{SO}_4)_2$		$(\text{NH}_4)_3\text{Fe}(\text{SO}_4)_3$ $\text{NH}_4\text{Fe}(\text{SO}_4)_2$

4.1.2 Experience At Kurabo's Hirakata Plant

Plant Description

This plant is a development unit for Kurabo's SCR process and is capable of treating $30,000 \text{ Nm}^3/\text{hr}$ of flue gas. The unit is installed on an industrial boiler firing high-sulfur oil. Flue gas from the boiler contains 1500 ppm SO_x (40 ppm SO_3) and 280 ppm NO_x .

Figure 4-2 presents a schematic of the air preheater-SCR system. Flue gas from the boiler goes directly to the SCR reactor. Ammonia is injected just upstream of the reactor at a rate of approximately one mole per mole NO_x . This results in a 90 percent reduction in NO_x emissions from the boiler. Flue gas exits the reactor at about 400°C , passes through a tubular-type air preheater and is discharged to the stack at about 220°C . Heat is exchanged with combustion air which enters the air preheater at 80°C and is discharged to the boiler at 230°C .

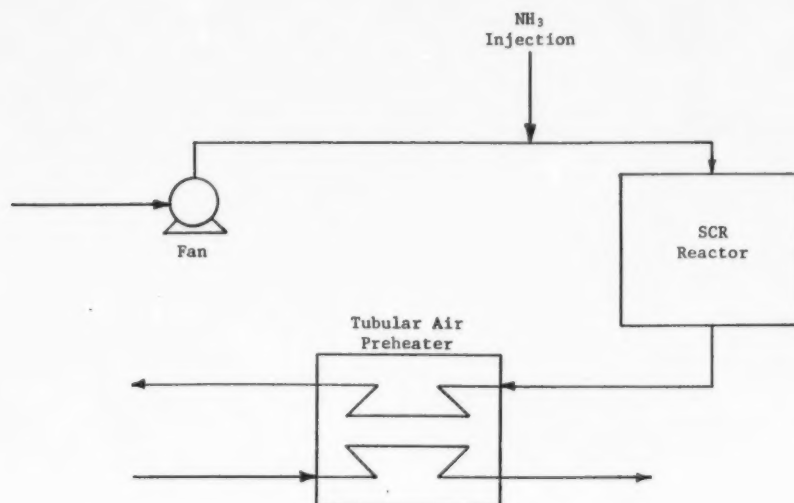


Figure 4-2. Selective Catalytic Reduction System At Kurabo's Hirakata Plant

Operating Experience

Kurabo expected deposit formation to occur in the air preheater prior to start-up of the plant. In an effort to prevent this from becoming a significant problem, a micro-computer system was installed to control the NH_3 injection rate. During normal operation of the unit, the NH_3 injection control system maintains the leak NH_3 concentration at or below 3 ppm.

Typically only a small quantity of deposits have been observed in the low temperature zone (below 190°C) of the air preheater while the high-temperature zones are deposit free and no increase in pressure drop has occurred. However, during upset conditions, the NH_3 emissions have exceeded 10 ppm and a considerable amount of deposits formed causing a considerable increase in the pressure drop through the air preheater. No information is available on how the air preheater is cleaned or on the time required for cleaning.

It appears that the low NH_3 emissions are the major factor in controlling air preheater plugging. However, evidence indicates that the relatively high flue gas exit temperature is also a factor. Kurabo has observed that when NH_3 injection is initiated shortly after start-up of the boiler and the gas temperature is relatively low, a considerable amount of deposits have formed in the air preheater.

Corrosion Of the Air Preheater

No quantitative measurement of air preheater corrosion has been conducted at Kurabo's plant and only a partial analysis of deposits has been reported. Table 4.3 presents available data on deposits found in the air preheater. As shown, the principal components of deposits are NH_3 and Fe. The anions associated with these cations are presumed to be sulfate ($\text{SO}_4^{=}$). The presence of Fe in the deposits is evidence of corrosion of the air preheater. The corrosion products should be similar to those found at Shindaikyowa Petrochemical's plant.

Table 4-3. ANALYSIS OF DEPOSITS FOUND IN THE AIR PREHEATER

Composition of Deposit							
Component	NH_3	Al	Fe	Cr	V	Cu	Ni
Quantity (mg/g)	50.5	0.15	200.0	1.7	0.43	0.33	0.93

4.1.3 Experience At Nippon Yakin's Kawasaki Plant

Plant Description

This plant has a small SCR unit ($15,000 \text{ Nm}^3/\text{hr}$ - $9,300 \text{ scfm}$) followed by a sodium based scrubber. Both systems were constructed by Mitsubishi ,

Kakoki Kaisha (MKK) and are operated commercially. The pollution control system has been retrofitted to treat a portion of the flue gas from two oil-fired industrial boilers. Flue gas from the boiler contains approximately 600-900 ppm SO_x (20-30 ppm SO_3) and 100-180 ppm NO_x .

Figure 4-3 is a schematic of the pollution control system at Nippon Yakin's plant. Flue gas from the boiler enters the low temperature side of a Rothemuehle air preheater where the temperature is raised from about 250°C to 345°C by heat exchange with gas from the reactor outlet. The gas is further heated to 385°C in a supplementary oil-fired heater and then enters the SCR reactor. Ammonia is injected just upstream of the reactor and approximately an 80 percent reduction in NO_x emissions is achieved. Flue gas discharged from the reactor passes through the high-temperature side of the air heater and is cooled to 270-320°C. The cooled gas enters the sodium-scrubber where approximately 90 percent of the SO_2 is removed. The flue gas is then discharged through a stack.

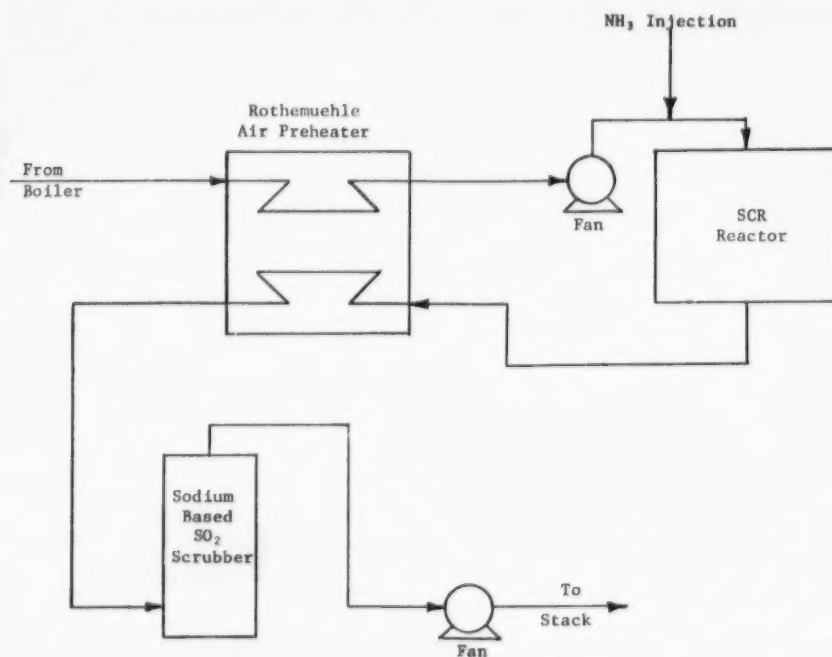


Figure 4-3. Pollution control system at Nippon Yakin's Kawasaki Plant.

Operating Experience

Under typical air preheater operating conditions, the NH_3 (10-20 ppm) and SO_3 (20-30 ppm) concentrations in the gas exiting the reactor would be expected to result in deposit formation in the air preheater. However, the relatively high gas temperature at the air preheater exit (270 - 320°C), is above the theoretical formation temperature of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ and no problems have been encountered. It is not clear from Ando's survey if the plant was originally designed to operate by discharging gas at 270 - 320°C or if plant operation was modified specifically to prevent deposit formation in the air preheater. However, operating experience at this plant does indicate that deposit formation can be prevented by raising the flue gas discharge temperature from the air preheater.

4.1.4 Experience At Chubu Electric's Chita Station

Plant Description

This plant has been the site of a large scale test of selective non-catalytic reduction using NH_3 injection. The ammonia injection system for SNR was constructed by Mitsubishi Heavy Industries under a license agreement with Mitsubishi Chemical Industries and Exxon. The plant has the capacity for treating 1,050,000 Nm^3/hr (653,000 scfm) of flue gas from a boiler firing 0.2 percent sulfur oil. In the absence of SNR, the flue gas contains 120-140 ppm NO_x and 100 ppm SO_x (2-3 ppm SO_3).

At Chubu Electric's plant, ammonia is injected in the boiler at a rate of 1.2 to 2.0 moles per mole of NO_x in the flue gas and a 40 to 50 percent reduction in NO_x emissions is achieved. The flue gas exits the boiler, passes through a Ljungstrom air preheater, and is discharged to the stack. No data are available on the flue gas temperatures in and out

of the air preheater. However, since this plant is a large (375 MW) boiler, it seems reasonable to assume temperatures are similar to those encountered in typical utility applications in the United States (i.e., 300 to 400°C in and 130 to 160°C out).

Operating Experience

Prior to installation and operation of the SNR system, the flue gas pressure drop through the air preheater was approximately 0.07 kPa (3.9 in H₂O). After NH₃ injection was initiated, the pressure drop began to increase and after two months of continuous operation, it reached 1.27 kPa (5.1 in H₂O). The plant was then shut down for several days and the air preheater was washed with water to remove the deposits.

After the initial experience with plugging of the air preheater, soot-blowing has been applied in an attempt to reduce the amount of deposits formed. This has met with limited success but water washing of the air preheater is still required about every six months.

Corrosion Of the Air Preheater

No quantitative measurement of air preheater corrosion has been conducted at Chubu Electric's Chita Plant. However, Ando did obtain samples of the deposits found in the air preheater and analyzed them by x-ray diffraction. The results of this semi-quantitative analysis are presented in Table 4-4. As shown, the majority of the deposits consist of unburned carbon. Other compounds in the deposits include ammonium sulfate and ammonium-iron-sulfate compounds. An examination of the deposit analysis indicates some corrosion of the air preheater did occur. However the amount of corrosion products found in the deposits indicates that corrosion is not extensive.

TABLE 4-4. ANALYSES OF DEPOSITS FOUND IN THE AIR PREHEATER
AT CHUBU ELECTRIC'S CHITA STATION

Deposit Location	Relative Amount of Compounds Found		
	Major	Medium	Minor
Low Temperature Zone (cold end)	Carbon	$(\text{NH}_4)_2\text{SO}_4$	--
Low Temperature Zone (hot end)	Carbon	$(\text{NH}_4)_2\text{SO}_4$	$(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$
Intermediate Temperature Zone (cold end)	Carbon	$(\text{NH}_4)_2\text{SO}_4$	$(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$
Intermediate Temperature Zone (intermediate)	Carbon	$(\text{NH}_4)_3\text{Fe}(\text{SO}_4)_3$	$(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$
Intermediate Temperature Zone (hot end)	Carbon	$\text{NH}_4\text{Fe}(\text{SO}_4)_2$	$(\text{NH}_4)_3\text{Fe}(\text{SO}_4)_3$
High Temperature Zone (cold end)	Carbon	$\text{NH}_4\text{Fe}(\text{SO}_4)_2$	$(\text{NH}_4)_3\text{Fe}(\text{SO}_4)_3$
High Temperature Zone (hot end)	Carbon	$\text{NH}_4\text{Fe}(\text{SO}_4)_2$	--

4.1.5 Experience at Mitsui Petrochemical's Chiba Plant (SNR)

Plant Description

A selective non-catalytic reduction system, supplied by Tonen Technology, is installed on an oil fired industrial boiler at Mitsui Petrochemical's Chiba Plant. The boiler currently fires 0.02 percent sulfur oil although 0.8 percent sulfur oil was fired when the SNR system was first installed. The NH_3 injection rate is approximately 2.0 moles of NH_3 per mole of NO_x and a 35 to 40 percent reduction in NO_x emissions is achieved with an NH_3 emission rate of 10-20 ppm.

Flue gas from the boiler passes through a conventional Ljungstrom air preheater and discharges to the stack. No data are available on flue gas NO_x concentration or temperatures in and out of the air preheater.

Operating Experience

The SNR system began operation in 1976. At this time the boiler was firing 0.8 percent sulfur oil which corresponds to an estimated 10 to 15 ppm SO₃. In addition, a higher NH₃ injection rate was used to achieve a 45 percent reduction in NO_x emissions with an NH₃ emission rate of 20 to 30 ppm. After several weeks of operation the air preheater plugged and required cleaning. Unfortunately no data are available on the type of cleaning procedure used or the time required for cleaning.

After the initial experience with air preheater plugging, distillate oil has been fired in the boiler. In addition, the NH₃ injection rate was reduced with a consequent reduction in the NH₃ emission rate to 10 to 20 ppm. Since this time, no deposits or plugging of the air preheater have been observed.

4.1.6 Experience At Mitsui Petrochemical's Chiba Plant

Plant Description

An SCR system is installed on an oil-fired industrial boiler at Mitsui Petrochemical's Chiba Plant. This system was designed by Mitsui Engineering and is capable of treating 200,000 Nm³/hr of flue gas. The boiler fires 0.2 to 0.3 percent sulfur oil and the flue gas contains an estimated 3 to 6 ppm SO₃. Ammonia is injected upstream of the reactor and approximately 90 percent of the NO_x is reduced with NH₃ emissions at or below 5 ppm. No data are available on the flue gas NO_x concentrations.

Flue gas from the reactor passes through an air preheater and is discharged to the stack. No information is available on the flue gas temperatures in and out of the air preheater or on the type of air preheater employed.

Operating Experience

The SCR system began operation in 1975 and has not experienced any plugging problem. Presumably this is due to the low NH_3 and SO_3 concentrations which correspond to formation temperatures of approximately 165°C for NH_4HSO_4 and 195°C for $(\text{NH}_4)_2\text{SO}_4$. It is also possible that elevated flue gas temperatures (above 195°C) could be responsible for the absence of deposits.

4.1.7 Experience At EPDC's Air Preheater Test Facility, Takasago Station

Plant Description

A test facility was set-up specifically to examine deposit formation, plugging, and corrosion of air preheaters due to the presence of unreacted NH_3 in flue gas. EPDC installed a Ljungstrom air preheater to process a slipstream of flue gas from a coal-fired boiler. The air preheater was sized for $9000 \text{ Nm}^3/\text{hr}$ (5600 scfm) of flue gas. Several materials of construction and configurations of the heat transfer elements were evaluated.⁸

Figure 4-4 is a schematic of the test facility. Flue gas is withdrawn from the boiler downstream of the economizer. At this point the gas temperature is 290°C , particulate loading is about 10 g/Nm^3 (4.1 gr/scf), and the SO_3 concentration ranges from 1 to 20 ppm. The Japanese investigators (Y. Nakabayashi and K. Mouri) cited difficulties in measuring the SO_3 concentration so an average value was not reported.

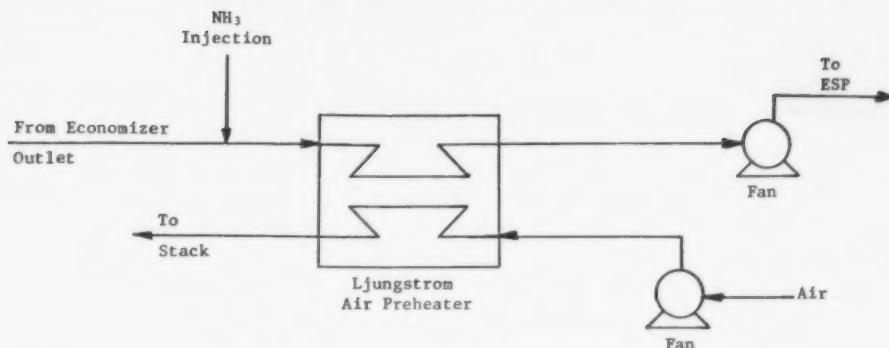


Figure 4-4. Schematic of EPDC's air preheater test facility.

Ammonia was injected into the flue gas which was cooled from 290 to 140°C in the air preheater. The NH_3 injection rate was controlled to maintain an air preheater inlet concentration of 20 ppm for the first 480 hours of the test and 50 ppm for the final 3,240 hours.

Operating Experience

The air preheater test unit was operated a total of 3,720 hours and was inspected approximately once every month. During the test period the pressure drop on the flue gas side of the air preheater increased from 1.2 to 1.67 kPa (4.8 to 6.7 in H_2O) as shown in Figure 4-5. Throughout the entire test period, the heat transfer efficiency of the air preheater was not impaired.

Figure 4-5 indicates that the pressure drop and presumably, the quantity of deposits gradually increased during the test program. The majority of deposits were found at the cold end of the intermediate temperature zone in the air preheater. The investigators estimated that between 30 and 40 percent of the crosssectional area open to flow was blocked at the conclusion of the test program.

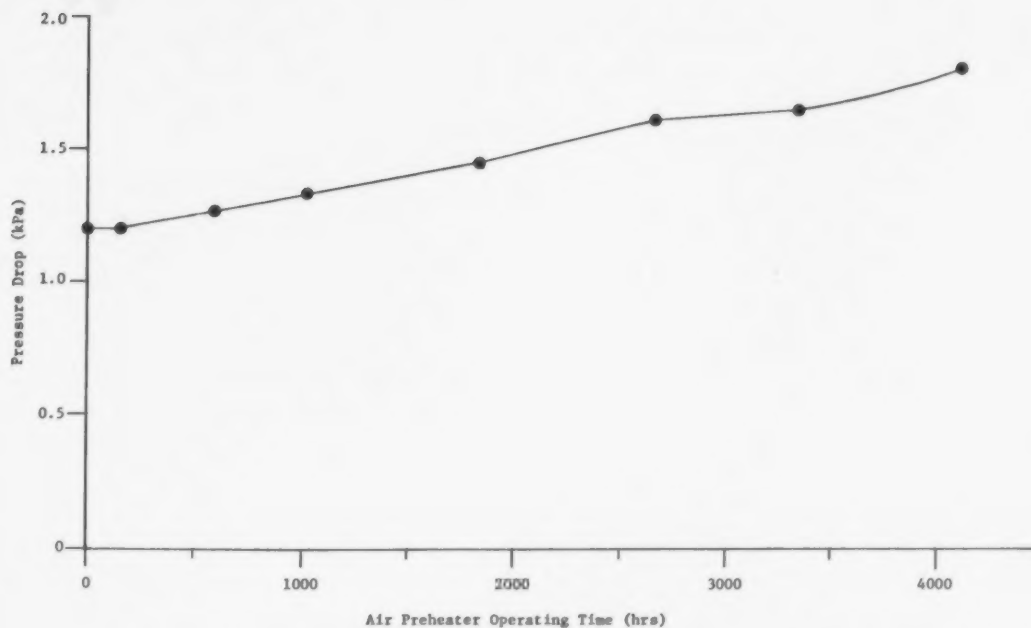


Figure 4-5. Air preheater pressure drop vs. operating time.

After the initial tests, an ESP was operated upstream of the air preheater to remove particulates from the flue gas. During these tests, the rate of deposition and plugging was much more rapid. The investigators concluded that particulates had a cleaning effect on the deposits. However, it is also possible that particulates act as condensation sites and thereby prevent deposit formation on the preheater surfaces.

Corrosion Of the Air Preheater

Corrosion, as evidenced by a reduction in heat transfer element thickness, was examined at each of the six inspections. The results of these examinations are presented in Figure 4-6. As shown, the most serious corrosion occurred at the cold end of the low temperature zone of the air preheater. A relatively minor reduction in element thickness was observed in the intermediate and high temperature zones, but the investigators attributed this to erosion by particulates rather than corrosion.

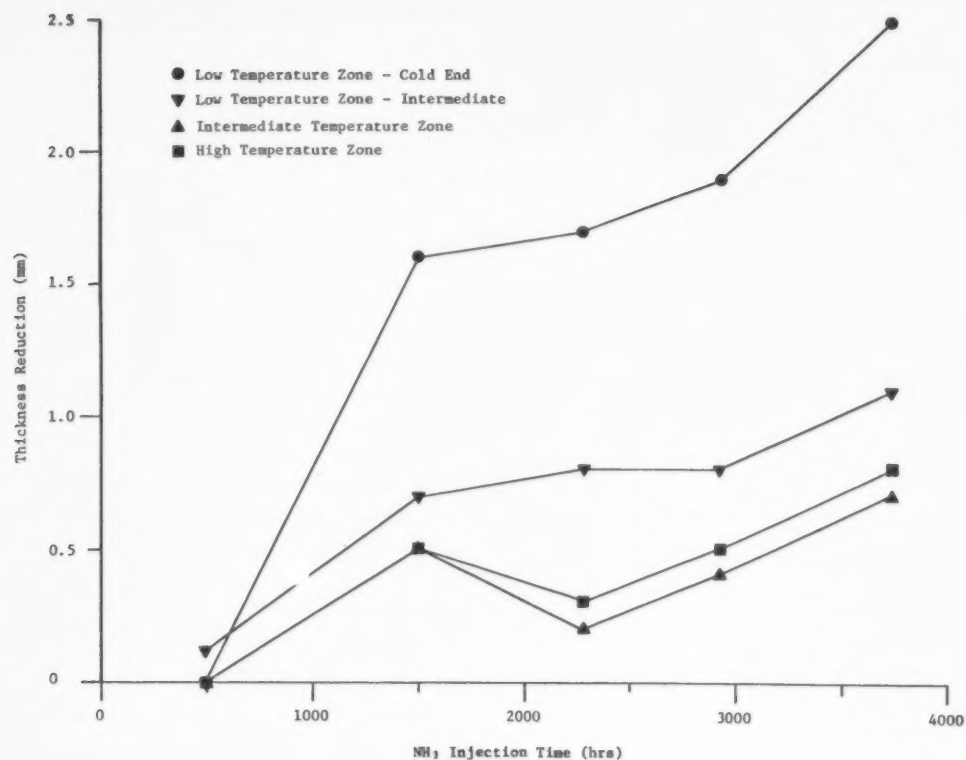


Figure 4-6. Corrosion of steel heat transfer elements.

After the third inspection (1496 hours), deposit samples were subjected to chemical and x-ray diffraction analyses. The results of these analyses are presented in Table 4-5. As shown, the principal components of the deposits are SiO_2 , Al_2O_3 and SO_4^{-2} . Each of these compounds are typically found in fly ash so it is reasonable to assume that the deposits are largely fly ash. Compounds identified by x-ray diffraction include the $\text{NH}_4\text{-Fe-SO}_4$ compounds found by Ando in his analysis of preheater deposits and in his laboratory tests (Section 3.3).

TABLE 4-5. ANALYSIS OF AIR PREHEATER DEPOSITS FROM EPDC'S TEST FACILITY

Compound	Steel Heat Transfer Elements				Enamel Coated Heat Transfer Elements					
	Intermediate Temperature Zone		Low Temperature Zone		Intermediate Temperature Zone		Low Temperature Zone			
	Hot End	Cold End	Hot End	Cold End	Hot End	Cold End	Hot End	Cold End	Hot End	Cold End
SiO ₂ (wt %)	-	33.9	25.3	20.0	-	31.5	24.2	27.9	-	-
Fe ₂ O ₃ (wt %)	-	7.4	14.3	39.0	-	4.7	4.4	7.1	-	-
Al ₂ O ₃ (wt %)	-	13.6	15.1	10.7	-	15.4	13.8	11.6	-	-
SO ₄ ⁻² (wt %)	-	21.4	26.8	5.2	-	30.6	34.4	8.7	-	-
NH ₄ ⁺ (wt %)	-	1.6	3.6	2.9	-	2.4	4.2	8.0	-	-
NH ₄ /SO ₄ mole ratio	-	0.4	0.7	3.0	-	0.4	0.65	4.9	-	-
NH ₄ FeSO ₄ •12H ₂ O	-	*	-	-	-	*	*	-	-	-
(NH ₄) ₂ S ₂ O ₈	-	*	-	-	-	*	*	-	-	-

*Identified by x-ray diffraction

4.1.8 Experience At Kawasaki Steel's Chiba Plant

Plant Description

The pollution control system at Kawasaki Steel's Chiba Plant is comprised of an ESP, a lime SO_2 scrubber, a wet ESP, and an SCR reactor. This system treats $850,000 \text{ Nm}^3/\text{hr}$ ($529,000 \text{ scfm}$) of off-gas from an iron-ore sintering operation. The SCR unit was manufactured by Hitachi Zosen and is operated to reduce about 90 percent of the NO_x in the gas stream.

Figure 4-7 is a schematic of the pollution control system. Off-gas from the sintering machine first passes through an ESP and then the lime scrubber where 90 percent of the SO_2 is removed. The scrubbed gas is then treated in a wet ESP which serves as a demister for the scrubber and also removes sulfuric acid from the gas. At this point the gas temperature is about 55°C . Prior to entering the SCR reactor, the gas is heated to 400°C by a supplementary heater, a Ljungstrom air preheater and a second heater. Ammonia is injected at a rate of 0.9 to 1.3 moles per mole of NO_x . The gas exits the reactor, is cooled in the air preheater to 170°C , and then discharged to the stack. At the air preheater inlet, the gas contains about 10 ppm NH_3 and 2 ppm SO_3 .

Operating Experience

Operation of the Ljungstrom air preheater in this system has not been impaired by deposition of ammonium salts. A small quantity of deposits have been observed but cleaning of the air preheater has not been required. This good performance record is attributed to the low SO_3 concentration in the flue gas.

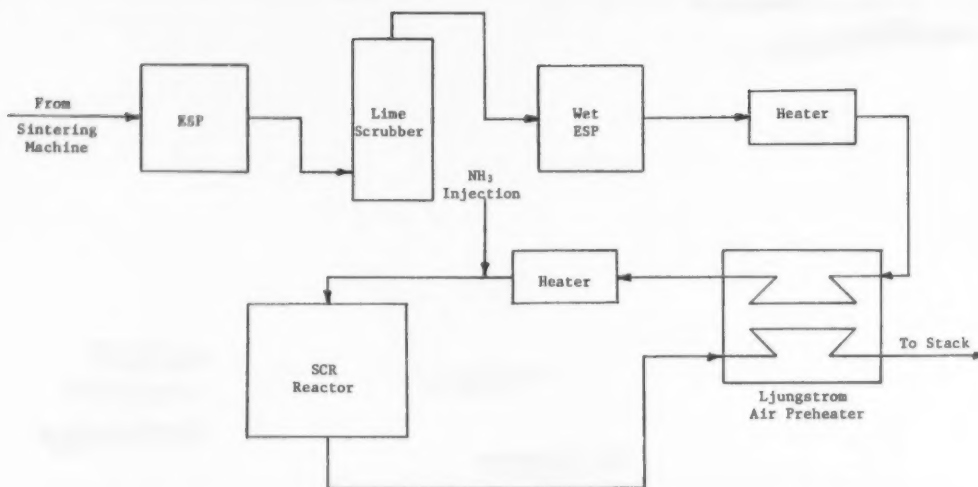


Figure 4-7. Schematic of Kawasaki Steel's Chiba Plant.

4.1.9 Experience at Nippon Steel's Nagoya Works

Plant Description

The JGC Corporation operated an SCR pilot plant (2,000 Nm³/hr-1250 scfm) at the Nagoya Works of Nippon Steel from May, 1976 to November 1977. During 1977, a Rothemuehle heat exchanger was installed and operated downstream of the SCR reactor. The pilot plant treated a slipstream of off-gas from an iron-ore sintering machine. The treated gas contained 100 to 200 ppm NO_x, 80 to 120 ppm SO_x (an estimated 5 to 15 ppm SO₃), and .12 to .15 g/Nm³ (.05 to .06 gr/scf) of particulates.

Figure 4-8 is a schematic of the SCR-air preheater system. Ammonia is injected upstream of the reactor at a rate of 1.1 to 1.5 moles per mole of NO_x and a 90 to 95 percent reduction in NO_x emissions is achieved. Gas leaves the reactor at 285°C and is cooled in the air preheater to 175°C.

The NH_3 concentration at the air preheater inlet is above 10 ppm and based on the NH_3/NO_x mole ratio at the reactor inlet, this concentration is estimated to range from 20 to 50 ppm.

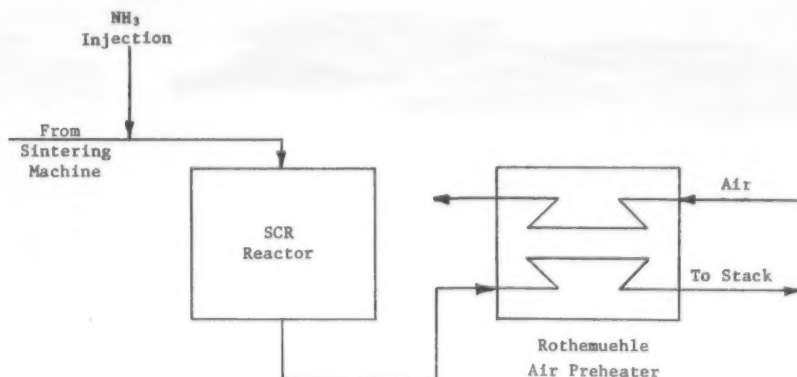


Figure 4-8. Schematic of the SCR system at Nippon Steel's Nagoya Works.

Operating Experience

Two tests were conducted to examine deposit formation and the performance of the air preheater. The first test lasted 1900 hours and the duration of the second was 2100 hours. During the first test, the gas side pressure drop increased from 0.82 to 2.1 kPa (3.3 to 8.5 in H_2O) and during the second test the pressure drop increased from 0.97 to 2.07 kPa (3.9 to 8.3 in H_2O). No information is available on how the preheater was cleaned between tests or how long the cleaning process took. Performance data indicate that the thermal efficiency of the air preheater was not impaired.

Corrosion of the Air Preheater

At the conclusion of the air preheater tests, corrosion of the elements was examined and the deposits were subjected to chemical analysis. Corrosion of the heat transfer elements was described as "minor". This good performance was attributed to a neutralizing effect of the particulates in the gas stream which contain Fe_2O_3 and CaO .

Table 4-6 presents the results of the chemical analysis of the deposits found in the air preheater. As shown, the principal components (on a wt. percent basis) are Fe (presumably from particulates) and SO_4 . The NH_4 to SO_4 mole ratios indicate that 23 to 44 percent of the sulfate may be present as NH_4HSO_4 , although the results of x-ray diffraction analyses do not indicate that $(\text{NH}_4)_2\text{SO}_4$ or NH_4HSO_4 are present as major components of the deposits.

TABLE 4-6. COMPOSITION OF DEPOSITS FOUND IN THE AIR PREHEATER
AT NIPPON STEEL'S NAGOYA WORKS

Deposit Location	Chemical Composition (%)				NH_4/SO_4 Mole Ratio	Major Compounds	Relative Amount of Deposit
	Fe	Ca	SO_4	NH_4			
Low Temperature Zone	38	6.9	13.1	0.9	0.39	$\text{Fe}_2\text{O}_3, \text{CaSO}_4$	1
Intermediate - Low	35	6.0	19.1	1.5	0.44	$\text{Fe}_2\text{O}_3, \text{CaSO}_4$	1
Intermediate - High	32	5.7	24.1	1.3	0.30	$\text{Fe}_2\text{O}_3, \text{CaSO}_4$	6
High Temperature Zone	33	6.3	21.7	0.9	0.23	$\text{Fe}_2\text{O}_3, \text{CaSO}_4$	1

4.1.10 Experience at Nakayama Steel's Funamachi Works

Plant Description

Niigata Engineering Company has constructed and operated an SCR pilot plant and a Ljungstrom air preheater at Nakayama Steel's Funamachi Works. This plant has a capacity for treating a $6000 \text{ Nm}^3/\text{hr}$ (3700 scfm) slipstream of off-gas from an iron-ore sintering machine. The gas treated by the pilot plant contains 130 to 200 ppm NO_x , 100 to 180 ppm SO_x (10-20 ppm SO_3), and .11 to .27 g/Nm^3 (.05 to .11 gr/scf) of particulates.

Figure 4-9 is a schematic of the SCR-air preheater system at the Funamachi Works. Ammonia is injected upstream of the reactor at a rate of 0.95 moles per mole of NO_x . The NH_3 emissions from the reactor are estimated at about 5 ppm although no data are available on the NO_x reduction efficiency. The gas exits the reactor, is cooled from $280\text{--}350^\circ\text{C}$ to $180\text{--}220^\circ\text{C}$ in the air preheater, and is then discharged to a stack.

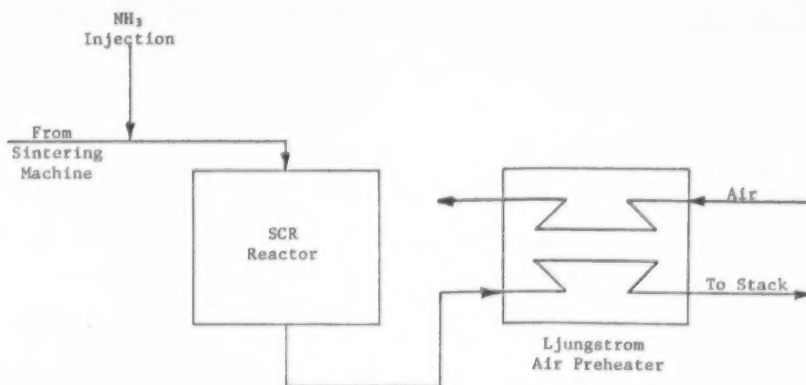


Figure 4-9. Schematic of SCR system at Nakayama Steel's Funamachi Works.

Operating Experience

The air preheater was operated for a total of 4000 hours. During the first 1800 hours of testing, soot blowing was employed and the gas side pressure drop remained nearly constant at 0.55 kPa (2.2 in H₂O). However, some deposits were found in the low temperature zone of the air preheater. These deposits were removed by water washing and the air preheater testing resumed.

For the final 2200 hours of testing the air preheater soot blowing system was not employed. During this period, the gas side pressure drop gradually increased from 0.55 to 0.82 kPa (2.2 to 3.3 in H₂O).

Corrosion of the Air Preheater

At the conclusion of the 4000 hour test period, the heat transfer elements were washed and weighed. The final weight was compared to the initial weight and the difference was assumed to be a result of corrosion. The results of this analysis are presented in Table 4-7. As shown, four materials were examined. Of these, the mild steel and COR-TEN experienced the greatest corrosion rates. However, these corrosion rates are considered to be minor. Again, a neutralizing effect due to the Fe₂O₃ and CaO in the particulates may have prevented more serious corrosion.

TABLE 4-7. WEIGHT LOSS OF HEAT TRANSFER ELEMENTS AT
NAKAYAMA STEEL'S FUNAMACHI WORKS

Heat Transfer Material	Weight Loss (%)
Mild Steel (SPC)	1.15
COR-TEN	0.91
Enamel Coated SPC	0.06
SUS 316	0.04

4.1.11 Experience at Chugoku Electric's Kudamatsu Station

Plant Description

At Chugoku Electric's Kudamatsu facility, the flue gas from boiler #2 (375 MW) and #3 (700 MW) is treated for NO_x by SCR systems supplied by IHI. The plant has an agreement with the city to limit total NO_x emissions below $154 \text{ Nm}^3/\text{hr}$. The de- NO_x system on the #2 boiler is a retrofit that consists of a single reactor which reduces NO_x from 160 ppm to <32 ppm. The #3 boiler included SCR in its initial design and consists of two parallel reactors which reduce the NO_x from 130 ppm to <26 ppm. Both boilers are fired with low sulfur oil.

The IHI de- NO_x systems are guaranteed for 80 percent removal at an NH_3/NO_x mole ratio of 0.90. Initially, the NO_x removal was 85 percent, but recently this has been reduced to 82 percent by using a mole ratio of 0.85. The #2 unit has operated for one year with no degradation and the plant manager is expecting at least one more year before catalyst replacement is necessary. Pressure drop through the reactor is 50 to 60 mmH_2O .

Operating Experience

There have been problems with air preheater pluggage by NH_4HSO_4 . On the #2 boiler, the air preheater has required washing every two months and the air preheaters on the #3 boiler have also required washing. The plant is trying to improve the soot blowing technique to minimize air preheater plugging. Normally the pressure drop is 100 mmH_2O , but washing is required when this increases to 300 $\text{mm H}_2\text{O}$. 5000 tons of water are required for one washing. Wash water containing the ammonium sulfates is stored and neutralized.

The flue gas conditions that lead to preheater plugging are <4 ppm NH_3 , 4 ppm SO_3 , and 100 to 110 ppm SO_2 at the outlet of the reactor. Gas exits the preheater at about 140°C . The deposits are experienced in the intermediate temperature zone.

Currently, they soot blow with air, but plan to switch to steam in order to avoid blowing the hot-side with cold gas and potentially causing deposits to form on the hot end elements. The low temperature side is blown once per shift and the high temperature side once per day. A soot blowing cycle consists of blowing for two hours with 1.37 MPa air. Previously, the high temperature side was blown only once per three days. Further improvements including going to higher diameter nozzles are planned in order to reduce required water washings to once every three months. Currently there are no data available on corrosion of the air preheater heat transfer elements.

4.1.12 Experience at Chugoku Electric's Shimoneski Power Station

Plant Description

Chugoku Electric's Shimoneski Power Station operates a 175 MW coal-fired boiler which has recently been retrofitted with an SCR system that began operation in April 1980. As such, this is the first commercial application of SCR technology to a coal-fired boiler. The SCR unit at Shimoneski is capable of treating 550,000 Nm³/hr (340,000 scfm) of flue gas and is designed for 50 percent NO_x removal. The reactors and catalyst charge, however, were sized for 80 percent removal to provide a conservative design and to help minimize NH₃ emissions. The gas entering the reactor contains 500 ppm NO_x and about 250 ppm NO_x at the reactor exit. NH₃ emissions average about 0.5 ppm with a maximum emission rate of 3.0 ppm for short periods.

During installation of the SCR system at Shimoneski, some modifications were made to the air preheater to avoid problems with deposition of ammonium sulfates. The intermediate temperature zone element was changed to a corrosion resistant material similar to the standard low temperature zone material and the element shape was changed from a double undulated to a notched plate type. Hot side soot blowers were also added.

Operating Experience

The SCR system began operation in April, 1980 at which time the boiler was firing low sulfur coal (0.5 - 0.6% sulfur). In mid-May, the boiler was shut down for inspection of the SCR system. At this time, both the SCR reactor and the air preheaters downstream of the reactor were found to be free of deposits. Since the boiler operation resumed, a medium-sulfur oil (1.5 - 2.0% sulfur) has been fired and the SCR system and downstream preheaters have operated without trouble. During operation of the SCR system, the air preheater soot blowers have been operated 4 times a day as a safety measure. However, since no deposit formation has been observed, the power company plans to reduce the soot blowing frequency. It appears that the low NH_3 emission rate, coupled with good control of the NH_3 injection rate, are responsible for the trouble-free operation.

4.1.13 Experience at Fuji Oil's Sodegaura Refinery

Plant Description

Fuji Oil currently operates an MHI SCR system on a low sulfur oil-fired steam generator in its Sodegaura refinery. The SCR system was designed as an integral part of the boiler and is installed in the duct work between the boiler and the economizer where the flue gas temperature ranges from 330 - 370°C. Flue gas flowrate from the boiler is estimated to be 280,000 Nm^3/hr (175,000 scfm) and contains approximately 115 ppm NO_x . Nearly 90 percent NO_x reduction is achieved in the reactor and the exit NO_x concentration is 15 ppm. No information is available on the NH_3 emissions from the reactor or the SO_3 concentration of the flue gas.

Operating Experience

The SCR system at Fuji Oil has operated for over 2½ years. After 6 months of operation, plugging was experienced in the economizer and a water wash was required. During this period the economizer pressure drop increased twelvefold. Operations personnel at Fuji Oil concluded this problem stemmed from some plug-

ging in the catalyst bed which caused the concentration of unreacted NH_3 in the reactor outlet gas to increase. This increased the reaction temperature for NH_4HSO_4 formation and allowed NH_4HSO_4 to form on the economizer tubes. Additional soot blowers were installed in the reactors and the soot blowing procedure for the reactor and economizer was changed. This allows the boiler to operate one year before the economizer must be cleaned. Soot blowing is done carefully to avoid contacting the catalyst with water droplets. No corrosion was observed in the economizer.

4.2 SUPPLEMENTARY EXPERIENCE WITH AIR PREHEATER PLUGGING, CORROSION, AND MAINTENANCE

Ammonia injection has been and is being used in conjunction with coal- and oil-fired boilers for purposes other than reduction of NO_x emissions. In the late 1950's, ammonia injection was first employed to reduce acid corrosion of air preheater surfaces by neutralizing SO_3 present in the flue gas.¹⁴ In the 1960's, ammonia injection was successfully employed to improve ESP performance by conditioning fly ash.^{15,16} There are several reports which document the results of NH_3 injection for each of these applications. This section summarizes the information from each of these reports which is applicable to $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition in air preheaters.

Table 4-8 presents a summary of the supplementary experience with NH_3 injection. The information presented in Table 4-8 relates only to instances where NH_3 has been injected upstream of an air preheater. As shown, the magnitude of the problem ranges from no deposit formation to severe pluggage of the air preheater. Unfortunately, the data presented in Table 4-8 are not complete since no flue gas SO_3 concentrations were reported by Baxter. This makes interpretation of the data difficult, particularly a quantitative analysis including calculation of $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 formation temperatures.

A qualitative examination of the data does support some of the trends exhibited by the data from Japanese experience. The magnitude of the plugging problem does increase as SO_3 concentration of the flue gas increases (Bankside vs. Widows Creek). In addition, high air preheater outlet tempera-

TABLE 4-8. SUMMARY OF EXPERIENCE DURING NH₃ INJECTION TESTS FOR CORROSION CONTROL AND FLY ASH CONDITIONING

Investigator(s)	Plant/Location	Application	Air Preheater Type	Flue Gas Temperature (°C)		NH ₃ at A.P.		SO ₂ at A.P.		Relative Severity of Deposit Formation
				A.P. Inlet	A.P. Outlet	Inlet (ppm)	Inlet (ppm)	Inlet (ppm)	Inlet (ppm)	
J.T.S. Gundry, B. Lees, L.K. Rendle, E.J. Wicks	Bankside Generating Station, Great Britain	Corrosion Reduction	Tubular	230	150	30	30	7	7	Moderate
J.T. Reese, J. Greco	TVA Widows Creek - Unit 7	Fly Ash Conditioning	Ljungstrom	340-370	130	15	15	30	30	Severe
W.A. Baxter	Station A Pulverized Coal-Fired	Fly Ash Conditioning	-	360	205	15	15	-	(low sulfur coal)	None
W.A. Baxter	Station B Pulverized Coal-Fired	Fly Ash Conditioning	-	370	150	15	15	-	(low sulfur coal)	Severe
W.A. Baxter	Station C Pulverized Coal-Fired	Fly Ash Conditioning	-	370	145	15	15	-	(medium sulfur coal)	Moderate
W.A. Baxter	Station D Pulverized Coal-Fired	Fly Ash Conditioning	-	400	225	15	15	-	(medium sulfur coal)	None
R. Kato, B.E. Paris	B.E. Morrow Plant Consumers Power Pulverized Coal-Fired	Corrosion Reduction	Tubular	215	154	100*	100*	-	(4% sulfur coal)	None Detected

*NH₃ was injected at a rate of 0.06% by weight of fuel - this is estimated flue gas NH₃ concentration based on data in report.

tures tend to minimize or eliminate deposit formation in the air preheater as evidenced by plants A and D in Baxter's study.

To provide a more thorough understanding of the circumstances surrounding the work summarized in Table 4-8, a brief description of each of the plants is included in this section. This description includes a summary of pertinent data and a discussion of the operating experiences at each installation. Where appropriate, a qualitative analysis of the operating experience is presented.

4.2.1 Experience At Bankside Generating Station, United Kingdom

Plant Description

The generating station consists of four, 36 MW boilers firing high-sulfur oil (3.5 to 3.8 percent sulfur). Soon after start-up, extensive corrosion of the primary air preheater was encountered. In an effort to alleviate this problem, an ammonia injection system was installed between the secondary (flue gas temperature = 230°C) and the primary air preheaters on one of the units. Ammonia was injected at a rate of 0.06 percent by weight of the fuel (an estimated 30 ppm).

Operating Experience

Prior installation of NH₃ injection equipment at the Bankside station, other researchers had conducted tests which indicated NH₃ could be effective in controlling acid corrosion. Therefore a series of short term tests were conducted followed by a 3000 hour, long-term test.

During the short term tests (approximately two weeks long), investigators observed an increase in deposits in the low temperature zone of the air preheater. Typically, the gas side pressure drop would increase from 0.20 to 0.25 kPa (0.8 to 1.0 in H₂O) during these tests. Water washing was used and found to be satisfactory for removing deposits. In subsequent

tests, shot cleaning was used instead of water washing and this has proven effective in controlling build-up of deposits in the air preheater.

Corrosion of the Air Preheater

At the Bankside Generating station, NH_3 injection has been successfully employed to reduce air preheater corrosion. Analysis of the water used for washing the air preheater indicated that a 73 percent reduction in corrosion (as evidenced by iron concentration in the water) is attributable to NH_3 injection. Results of the long-term (3000 hour) test have shown that the service life of the air preheater is increased from 3 years to an estimated 12 years due to NH_3 injection. As a result of this test, permanent NH_3 injection equipment was installed on all four of the boilers at the Bankside station.

4.2.2 Experience At TVA's Widows Creek Unit 7¹⁵

Plant Description

Widows Creek Unit 7 is a 550 MW coal-fired boiler which was equipped with four air preheater-ESP trains. Shortly after installation of the ESP's, collection efficiency dropped from the design level of 90 percent to below 60 percent. In an effort to improve performance of the ESP's, a pilot NH_3 injection system was installed to treat the flue gas entering one of the ESP's on Unit 7. NH_3 was injected just upstream of the air preheater. At this point, flue gas temperature ranged from 340 to 370°C. An excess of NH_3 was injected during the initial tests (60 ppm NH_3) but this was later reduced to 15 ppm. Flue gas was cooled to approximately 130°C in the air preheater.

Operating Experience

Previous investigators had determined that ESP performance could be improved by conditioning of fly ash with ammonia. Initial tests on Unit 7 resulted in an increase in ESP efficiency from below 60 percent to approxi-

mately 97 percent at an NH_3 injection rate equivalent to 60 ppm in the flue gas. Subsequent tests indicated that NH_3 injection could be lowered to 15 ppm while maintaining ESP efficiency above 90 percent.

Based on the success of the initial NH_3 injection tests, provisions were made for permanent NH_3 injection on units 7 and 8. Once this equipment was installed, NH_3 injection was started on unit 7 at a rate equivalent to 15 ppm NH_3 in the flue gas. After several hours of operation an increase in the pressure drop across the air preheaters was observed and NH_3 injection was discontinued. The air preheaters were then cleaned by repeated sootblowing and a test was conducted to document NH_3 injection as the cause of the air preheater plugging.

NH_3 was injected upstream of air preheater B on unit 7 while air preheaters A, C, and D served as controls. After 24 hours, the pressure drop on air preheater B was 1.80 kPa (7.2 in H_2O) while the pressure drop across A, C, and D remained constant at 0.50 to 0.75 kPa (2 to 3 in H_2O). As a result of this test, the NH_3 injection equipment was moved downstream of the air preheaters.

No corrosion was observed during the tests with NH_3 injection upstream of the air preheater.

4.2.3 Experience at Station A¹⁶

Plant Description

This station was one of four at which NH_3 injection for fly ash conditioning was studied by Koppers Company, Inc. Tests at Station A were conducted on a small pulverized coal-fired boiler burning a low-volatile, low-sulfur, high-ash coal. NH_3 was injected upstream of the air preheater at a rate equivalent to 15 ppm NH_3 in the flue gas. The flue gas was cooled

from 360 to 205°C in the air preheater, treated in an ESP, and then discharged to the stack.

Operating Experience

Initially SO₃ was injected into the flue gas to condition the ash but the results were unsatisfactory. Subsequently, NH₃ injection equipment was installed upstream of the air preheater and the ESP. At an injection rate equivalent to 15 ppm NH₃, particulate emissions from the ESP were reduced 85 percent. Analysis of the fly ash showed a decrease in resistivity and an increase in the pH of an aqueous ash slurry. No tendency to plug or raise the pressure drop in the air preheater was observed.

Permanent NH₃ injection equipment was then installed on Station A and at the time of Baxter's report, 11 months of trouble free operation had been recorded.

The absence of (NH₄)₂SO₄/NH₄HSO₄ deposits in the air preheater at Station A is probably due to the high flue gas temperature at the exit of the air preheater. Assuming an SO₃ concentration of 20 ppm (this should be high for a low-sulfur coal), the formation temperatures for (NH₄)₂SO₄ and NH₄HSO₄ are 205°C and 180°C, respectively. This indicates that the only potential for deposit formation might exist at the extreme cold end of the air preheater.

4.2.4 Experience at Station B¹⁶

Plant Description

Station B was the second NH₃ injection test by Koppers Company, Inc. The unit tested was a pulverized coal fired boiler burning medium volatile,

medium-ash, low-sulfur coal. NH_3 was injected upstream of the air preheater at a rate equivalent to 15 ppm in the flue gas. The flue gas was then cooled from 370 to 150°C in the air preheater, treated in an ESP, and discharged through the stack.

Operating Experience

The duration of the ammonia injection test program at Station B was very short. Almost immediately after NH_3 injection was initiated, pressure drop across the air preheater began to rise. This resulted in termination of the NH_3 injection tests. No data were reported which qualify the rate at which the pressure drop increased, or how the deposits were removed.

The obvious difference between Stations A and B is the flue gas temperature at the air preheater outlet (205°C vs. 150°C). However, since no data were reported on SO_3 concentration, it is uncertain which factors contributed to deposit formation in the air preheater.

4.2.5 Experience At Station C¹⁶

Plant Description

Ammonia injection tests were conducted at Station C on two identical cyclone-fired boilers burning high-volatile, low-ash, medium sulfur coal. NH_3 was injected upstream of the air preheater at a rate equivalent to 15 ppm in the flue gas. At the point of injection, flue gas temperature was 370°C. The flue gas was cooled in the air preheater to 145°C, treated by the ESP, and discharged to the stack. Each unit had a completely separate flue gas train.

Operating Experience

Although the two boilers tested at Station C were identical, the results

of the NH_3 injection tests were different in terms of fly ash conditioning. One unit responded well to NH_3 injection, exhibiting a 70 percent decrease in particulate emissions from the ESP. NH_3 injection on the other unit resulted in only a 30 percent reduction in emissions.

Although NH_3 injection had a varying impact on fly ash conditioning, deposit formation in the air preheaters of the two units appeared to be identical. Pressure drop across both air preheaters exhibited a gradual increase, although the rate was not as rapid as Station B. No information is available on the rate of increase or how the deposits were removed and, unfortunately, no data are available on the SO_3 concentration in the flue gas.

4.2.6 Experience At Station D¹⁶

Plant Description

Ammonia injection tests at Station D were conducted on a small, pulverized coal-fired boiler which burns low volatile, high ash, medium sulfur coal. Ammonia was injected upstream of the air preheater at a rate equivalent to 15 ppm in the flue gas. The gas temperature at the air preheater entrance was 400°C and was reduced to 225°C at the exit. Flue gas leaving the air preheater was treated in an ESP and then discharged to the stack.

Operating Experience

The NH_3 injection tests at Station D resulted in a significant improvement in ESP performance. Particulate emissions from the precipitator were reduced by 60 percent. No change in the air preheater pressure drop was observed during the test program. The lack of deposit formation is probably due to the high (225°C) temperature at the air preheater exit. Unfortunately, no data are available on the SO_3 concentration in the flue gas.

4.2.7 Experience at Consumers Power Co's B.E. Morrow Plant¹⁷

R. Kato and B.E. Paris conducted NH_3 injection tests on the pulverized coal-fired unit No. 1 of the B.E. Morrow plant operated by Consumers Power Co. The objective of these tests was to determine the ability of NH_3 to control or minimize H_2SO_4 corrosion. During the tests, the boiler operated at a steam rate of 320,000 lb/hr with an estimated flue gas flowrate of 135,000 Nm^3/hr (84,000 scfm). NH_3 was injected upstream of the air preheater at a rate equal to 0.06 percent by weight of the fuel flowrate which is equivalent to about 100 ppm in the flue gas. Corrosion rates were measured in the preheater using cooled corrosion probes.

Operating Experience

Two 30-hr tests were conducted in which NH_3 was injected into the preheater. Corrosion rates were measured with and without NH_3 injection and it was found that corrosion of the probes was virtually eliminated during the NH_3 injection tests. During NH_3 injection frequent checks were made of the gas-side pressure drop across the preheater and no increase was observed over the 60 hr period of NH_3 injection.

The fact that no change in preheater pressure drop was observed is in apparent conflict with the excessively high NH_3 injection rate. However, it should be noted that (1) the total NH_3 injection time was only 60 hours which is a very short time for deposition to cause preheater plugging. This is especially true in a tubular preheater which typically has larger gas passages than a regenerative preheater, and (2) if the NH_3 injection tests were not consecutive, deposits formed during the first test would decompose since NH_3 and SO_3 have a measurable vapor pressure over $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ at air preheater operating temperatures.

SECTION 5

THERMODYNAMIC AND KINETIC ANALYSES OF $(\text{NH}_4)_2\text{SO}_4$ / NH_4HSO_4 FORMATION IN AIR PREHEATERS

Ammonia emitted from SCR and SNR systems can react with SO_3 to form $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 which can deposit in and cause plugging and corrosion of air preheaters. If this occurs, it can increase the maintenance burden and potentially decrease the service life of the air preheater. Ultimately, formation of deposits in the preheater can impact the reliability of the boiler.

Reports of air preheater operating experience, in which the flue gas entering the preheater contained NH_3 , indicate that the magnitude of the deposition problem can range from no observable impact to rapid plugging of the preheater. In some cases, the reasons why deposit formation occurs are obvious (e.g., high NH_3 and SO_3 concentrations at the preheater entrance). However, in other cases, the causes of formation are unclear and cannot be fully explained with available data.

One objective of this study was to attempt to quantify the factors which influence and control formation of $(\text{NH}_4)_2\text{SO}_4$ / NH_4HSO_4 deposits. To achieve this objective, two types of analyses were conducted. First, the thermodynamics of NH_3 reactions were evaluated to identify which reactions can occur in the preheater and to quantify the extent of these reactions as a function of temperature and gas concentrations. Second, a kinetic analysis was conducted to identify the factors which control the rate of $(\text{NH}_4)_2\text{SO}_4$ / NH_4HSO_4 formation in the preheater. The combined results of these analyses will help define methods of preventing deposit formation in air preheaters.

This section discusses the approach used in conducting the thermodynamic and kinetic analyses and presents the results of these analyses (a detailed description appears in Appendices A and B). In addition, the results of the thermodynamic and kinetic analyses are discussed in terms of the operating data presented in Section 4.

5.1 THERMODYNAMIC ANALYSIS OF $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ REACTIONS

The formation of both $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 are temperature dependent reactions which proceed as a gas containing NH_3 , SO_3 , and H_2O is cooled. The temperature at which these reactions begin to occur will depend on the concentrations of reactants in the gas phase and on the product formed. In an effort to quantify the relationship between reactant concentrations, products formed, and temperature, a thermodynamic analysis of the $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 formation reactions was conducted. Specifically, the objectives of this analysis were:

- Identify what reactions can occur in the air preheater.
- Determine the conditions of concentration and temperature that result in formation of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ and, for given inlet NH_3 and SO_3 concentrations, the temperature at which compound formation begins.
- Identify the type and quantity of liquids/solid compounds formed at and below the initial formation temperature.

This analysis employed thermodynamic principles to determine which chemical reactions can occur in an air preheater and to estimate the equilibrium concentrations of both reactants and products. The results of the analysis do not imply that the reactions which can occur will proceed at a rapid or even measurable rate. They do, however, identify reactions which will not proceed under certain circumstances.

5.1.1 Approach

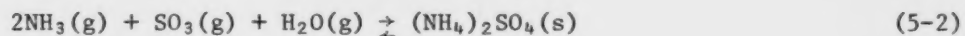
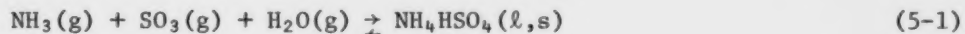
The first step in conducting the thermodynamic analysis required identification of NH_3 reactions which can occur at air preheater operating temperatures. Once the reactions of interest are identified, a more detailed analysis of the thermodynamic equilibrium can be conducted. Table 5-1 presents the formation temperatures for possible reaction products of NH_3 and other flue gas components. As shown, $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 , and NH_4Cl can form typical air preheater operating temperatures. For this study, NH_4Cl was not considered a significant reaction product. The reasons for this are that (1) no deposits of NH_4Cl have been found downstream of operating SCR systems, (2) the relatively low formation temperature of NH_4Cl will restrict its formation to the extreme cold end of the preheater which should not present a problem, and (3) assuming NH_3 reacts with H_2SO_4 before HCl , the NH_4Cl formation temperature will be below air preheater operating temperatures. This assumption appears to be valid since the kinetic analysis conducted as part of this study (Section 5.2) showed that the NH_3 - SO_3 reaction is very rapid.

TABLE 5-1. FORMATION TEMPERATURES FOR AMMONIUM COMPOUNDS
IN HYPOTHETICAL FLUE GAS

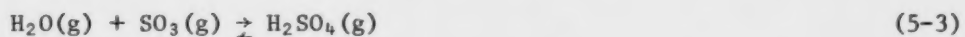
Flue gas component	Product	Formation temperature
CO_2	Ammonium carbonate	< - 6°C
CO_2	Ammonium bicarbonate	< - 21°C
SO_2	Ammonium sulfite	< 29°C
SO_2	Ammonium bisulfite	< 29°C
SO_3	Ammonium sulfate	< 210°C
SO_3	Ammonium bisulfate	< 185°C
NO	Ammonium nitrite	< - 160°C
NO_2	Ammonium nitrate	< 98°C
HCl	Ammonium chloride	< 150°C

The possibility of other $\text{NH}_3\text{-SO}_3$ compounds forming in the preheater was examined. Studies of the thermal decomposition of $(\text{NH}_4)_2\text{SO}_4$ indicated that ammonium pyrosulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_7]$ and sulfamic acid $(\text{NH}_2\text{SO}_3\text{H})$ can form at temperatures ranging from 150 to 200°C. However, these compounds were only detected during experiments in dry atmospheres and the presence of H_2O vapor was found to repress the formation of these compounds.¹⁸ Since flue gas typically contains about 10 percent H_2O , the formation of other $\text{NH}_3\text{-SO}_3$ compounds was not considered significant.

Based on this evaluation, the only chemical reaction products involving NH_3 and SO_3 that are expected to occur are:



In addition, another related chemical reaction must be considered.



The reaction shown in Equation 5-3 is significant from two standpoints. First, it will occur in the temperature ranges typical of an air preheater. Second, as the reaction proceeds, it lowers the concentration of SO_3 available for reaction with NH_3 (Equations 5-1, 5-2). Of course, NH_3 can react directly with $\text{H}_2\text{SO}_4(\text{g})$ to form $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 , but these reactions occur at a lower temperature than those represented by Equations 5-1 and 5-2. As a result, the analysis of thermodynamic equilibrium must consider the simultaneous equilibria of the $\text{NH}_3\text{-SO}_3$, $\text{NH}_3\text{-H}_2\text{SO}_4$, and the $\text{SO}_3\text{-H}_2\text{O}$ reactions.

The next step in conducting this analysis was to obtain the thermodynamic data required to predict the equilibrium constants for the $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 formation reactions. A literature search was conducted and Dr. Jumpei Ando was contacted. As a result, three sets of data were obtained which express the equilibrium constant (K) as a function of temperature. Figure

5-1 presents these equilibrium constants. As shown, the three relationships are quite similar.

The equilibrium expression selected for use in this analysis is the one developed by K. K. Kelley. This expression was selected because it falls in the middle of the range of available values presented in Figure 5-1. Dr. Ando's expressions had the highest equilibrium constant values for ammonium bisulfate and the lowest for ammonium sulfate. Scott and Cattell's expressions are at the other extreme, having the highest K for $(\text{NH}_4)_2\text{SO}_4$ and the lowest K for NH_4HSO_4 . The fact that the other thermodynamic data were at two opposite extremes also influenced the selection of Kelley's values as the data for this analysis.

The definition of the equilibrium constant is used in this analysis to determine equilibrium concentrations of products and reactants. For the $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 formation reactions, the following relationships apply:

$$K_{(\text{NH}_4)_2\text{SO}_4} = \frac{a_{(\text{NH}_4)_2\text{SO}_4}}{(\bar{f}_{\text{NH}_3})^2 (\bar{f}_{\text{SO}_3}) (\bar{f}_{\text{H}_2\text{O}})} \approx \frac{1}{(P_{\text{NH}_3})^2 (P_{\text{SO}_3}) (P_{\text{H}_2\text{O}})} \quad (5-4)$$

$$K_{\text{NH}_4\text{HSO}_4} = \frac{a_{\text{NH}_4\text{HSO}_4}}{(\bar{f}_{\text{NH}_3}) (\bar{f}_{\text{SO}_3}) (\bar{f}_{\text{H}_2\text{O}})} \approx \frac{1}{(P_{\text{NH}_3}) (P_{\text{SO}_3}) (P_{\text{H}_2\text{O}})} \quad (5-5)$$

where:

$\bar{f}_i$ = the partial fugacity of component i in a mixture

a_i = the activity of component i

P_i = the partial pressure of component i

The expression which relates the equilibrium constant to the activity and partial fugacities is the thermodynamically correct form. However, some simplifying assumptions can be made to express the equilibrium constant as a function of partial pressures. If the gaseous components are assumed to

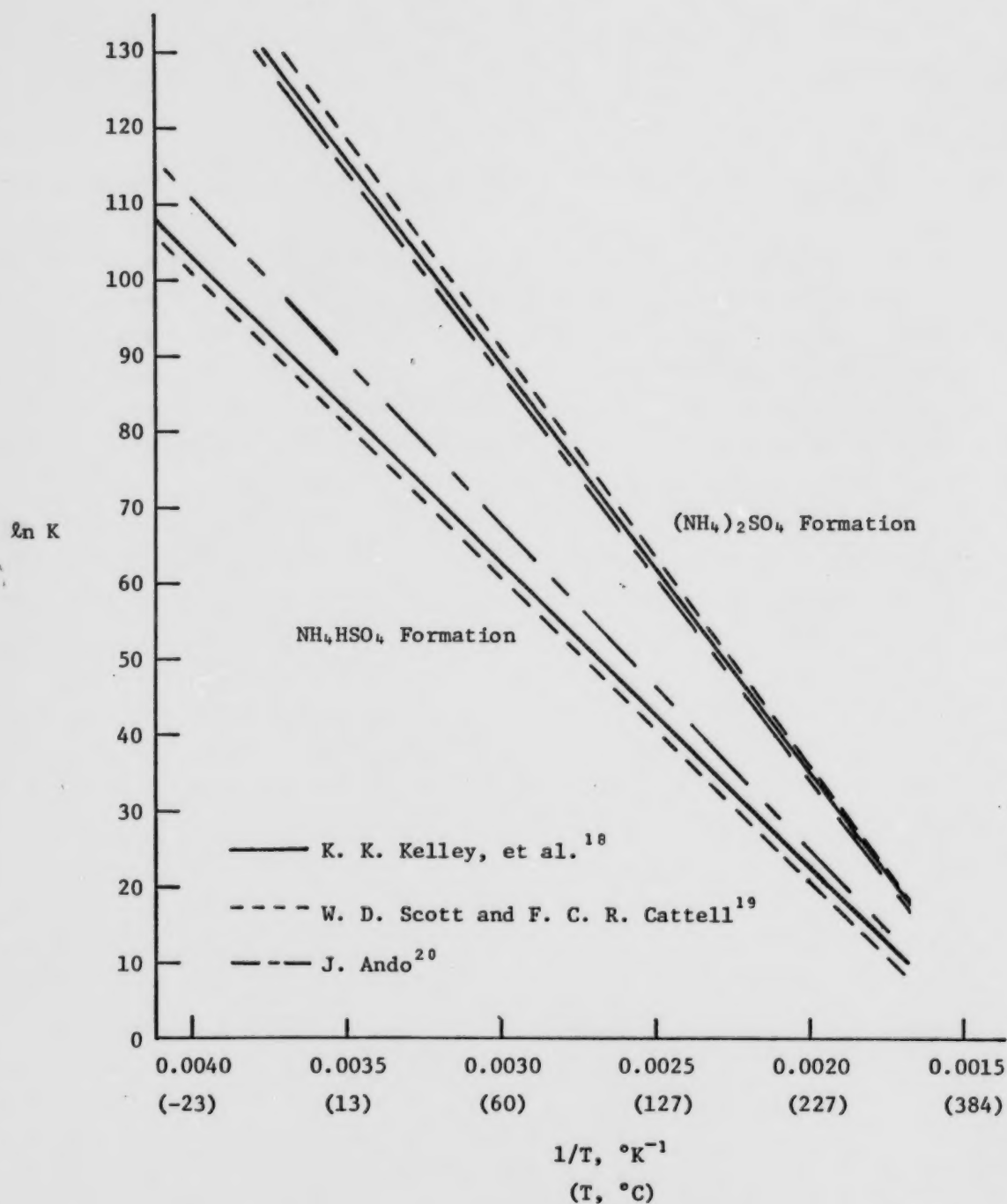


Figure 5-1. Equilibrium constants for ammonium sulfate and ammonium bisulfate formation.

behave as ideal gases, the partial fugacity of a component is equal to its partial pressure. At air preheater operating conditions, the assumption of ideal gas behavior for the three gaseous components is reasonable.

Another assumption made to simplify the equilibrium expression is that reaction products were formed as pure, separate condensed phases, and the activity of these products is equal to 1. This assumption was made because there was no data available on activities of ammonium bisulfate and ammonium sulfate in a mixture. This assumption does inject a small degree of uncertainty into the analysis since there is evidence indicating that $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 can form non-ideal solutions in which their activities may not equal 1. In order to estimate the possible impact of non-ideal solutions on the analysis, calculations were performed in which the activity was decreased by a factor of 10. The results of these calculations showed that a large change in the activity resulted in a relatively small change in formation temperature.

With the equilibrium expressions simplified, the data presented in Figure 5-1 can be used to predict equilibrium concentrations of NH_3 , SO_3 , $(\text{NH}_4)_2\text{SO}_4$, and NH_4HSO_4 . In order to consider formation of $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 , and the reaction of SO_3 and H_2O simultaneously, equilibrium concentrations were estimated using a technique based on the principle of free energy minimization. This technique relies on the fact that reactions proceed in a direction which causes a decrease in free energy. Therefore, the equilibrium state of a system is that state for which the total free energy is a minimum with respect to all possible changes (i.e., chemical reaction and mass transfer between phases) at a given temperature and pressure. This criterion for equilibrium can be used to predict equilibrium compositions in a system using the relationship between the equilibrium constant and free energy shown in Equation 5-6.

$$\ln K = - \frac{\Delta G_f}{RT} \quad (5-6)$$

where:

ΔG_f = free energy change of formation

R = gas law constant

T = temperature

Radian has developed a computer program which estimates the equilibrium composition of a system based on the principle of free energy minimization. The advantage of the free energy minimization methodology is its applicability to complex chemical systems without requiring the specification of reaction mechanisms. In this case, free energy minimization is advantageous since it permits simultaneous consideration of the equilibria between $\text{NH}_3\text{-SO}_3$, $\text{NH}_3\text{-H}_2\text{SO}_4$, and $\text{SO}_3\text{-H}_2\text{O}$. A more detailed discussion of this procedure is presented in Appendix A.

In order to use the free energy minimization program, the initial state of the system must be specified. In this case, the flue gas concentrations of NH_3 , SO_3 and H_2O were specified along with initial system temperature and pressure. The initial temperature was then reduced in steps and at each step, the free energy of the system was minimized. This resulted in equilibrium concentrations of NH_3 , SO_3 , H_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, and NH_4HSO_4 being determined as a function of temperature.

The initial flue gas concentrations which were examined using the free energy minimization technique include those listed in Table 5-2. These cases were selected primarily to reflect flue gas concentrations that could be encountered at the air preheater inlet, downstream of a NO_x SCR system. Ten ppm NH_3 is a reactor outlet concentration that might be expected from a typical SCR system operating as designed at 80-90 percent NO_x reduction. Thirty ppm NH_3 is a concentration that could result from a system designed for a smaller catalyst charge and/or larger NH_3/NO_x injection ratios. This level of ammonia in the SCR reactor outlet might also occur during a sudden load decrease on the boiler which could result in a temporary increase in

flue gas ammonia concentration before the process control equipment can respond.

TABLE 5-2. INITIAL FLUE GAS COMPOSITIONS FOR THERMODYNAMIC ANALYSIS

NH ₃ (ppm)	SO ₃ (ppm)	H ₂ O%
10	5	10
10	10	10
10	50	10
30	5	10
30	10	10
30	50	10
50	5	10
50	10	10
50	50	10
100	5	10
100	10	10
100	50	10
30	10	5
30	10	15

The 50 and 100 ppm NH₃ cases were included to demonstrate the effect of a large excess of ammonia on the system's thermodynamics. The SO₃ concentrations of 5 and 10 ppm were selected to represent typical coal and low-sulfur oil flue gas SO₃ concentrations. The 50 ppm SO₃ case was included to provide an upper limit for SO₃ concentrations that might result from burning a high sulfur fuel oil and to show the effect of a large excess of SO₃. The H₂O concentration in the flue gas was assumed to be 10 percent as this value is typical. For one NH₃/SO₃ combination, cases were evaluated at H₂O concentrations of 5 percent and 15 percent in the flue gas to check the influence of water vapor on the equilibrium concentrations. There was essentially no change in formation temperatures with change in H₂O concentration.

5.1.2 Results of the Thermodynamic Analysis

The thermodynamic analysis of $\text{NH}_3\text{-SO}_3$ reactions estimates the simultaneous equilibrium concentrations of the reactants (i.e., NH_3 and SO_3) and products (i.e., $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 , and H_2SO_4) as a function of temperature. The results of this analysis predict what compounds can form at a given set of conditions but they do not indicate the rate at which products are formed. Consequently, the discussion presented here considers reactions which are possible but which may not occur rapidly.

The initial result of the thermodynamic analysis (one that was unexpected in light of experimental data) is that $(\text{NH}_4)_2\text{SO}_4$ is the principal product at equilibrium for all the cases examined. The reason for this result is that, for a given temperature, the change in free energy for $(\text{NH}_4)_2\text{SO}_4$ formation is greater than the change in free energy for NH_4HSO_4 formation. While this may be true at equilibrium, it does not agree with the experimental results supplied by Dr. Ando which indicate that NH_4HSO_4 is often the principal compound found in deposits. Apparently the NH_4HSO_4 formation reaction occurs at a more rapid rate than the $(\text{NH}_4)_2\text{SO}_4$ formation reaction under the time-temperature history experienced by flue gas in an air preheater.

In order to predict equilibrium concentrations that are more representative of the reactions which can occur in an air preheater, the thermodynamic analysis was performed a second time. In the second analysis, NH_4HSO_4 and H_2SO_4 were specified as the only possible products and equilibrium concentrations were estimated. The combined results of the two sets of equilibrium calculations are presented in Figures 5-2, 5-3, and 5-4. These figures show the effects of changing inlet NH_3 concentration at constant inlet SO_3 concentrations of 5, 10, and 50 ppm, respectively.

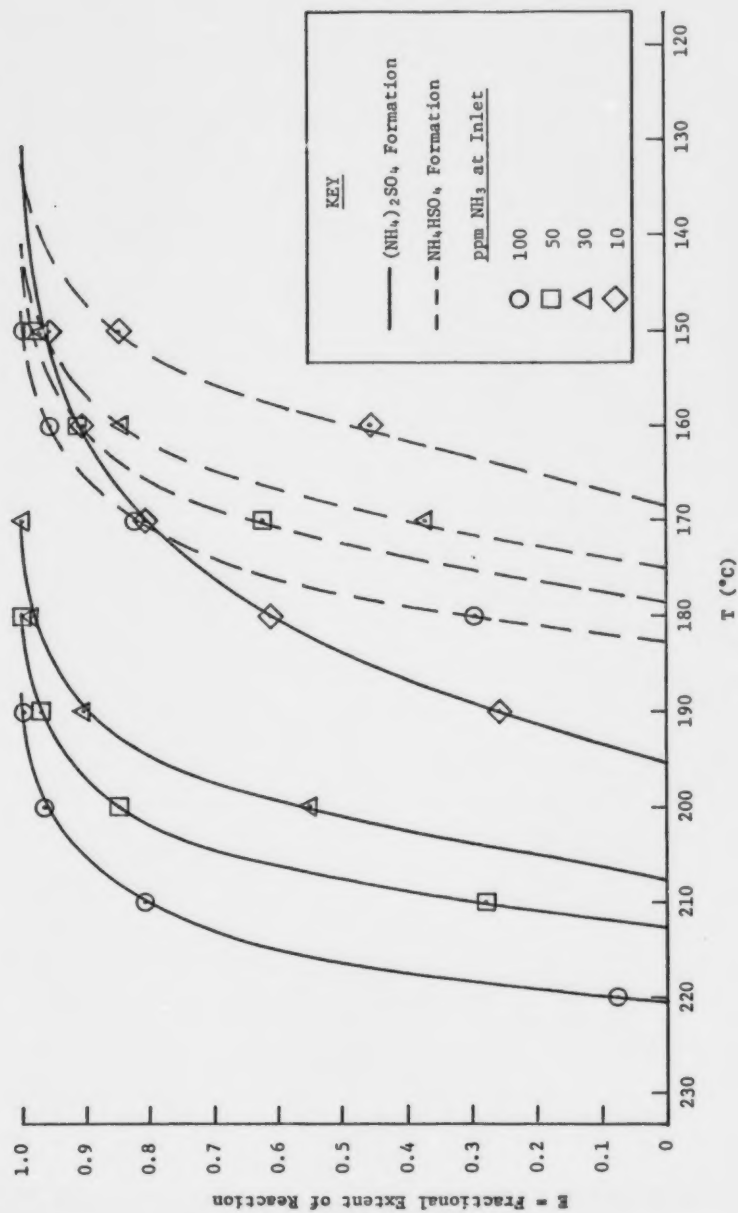


Figure 5-2. Thermodynamic equilibria for ammonium sulfate and ammonium bisulfate with 5 ppm SO₃ inlet.

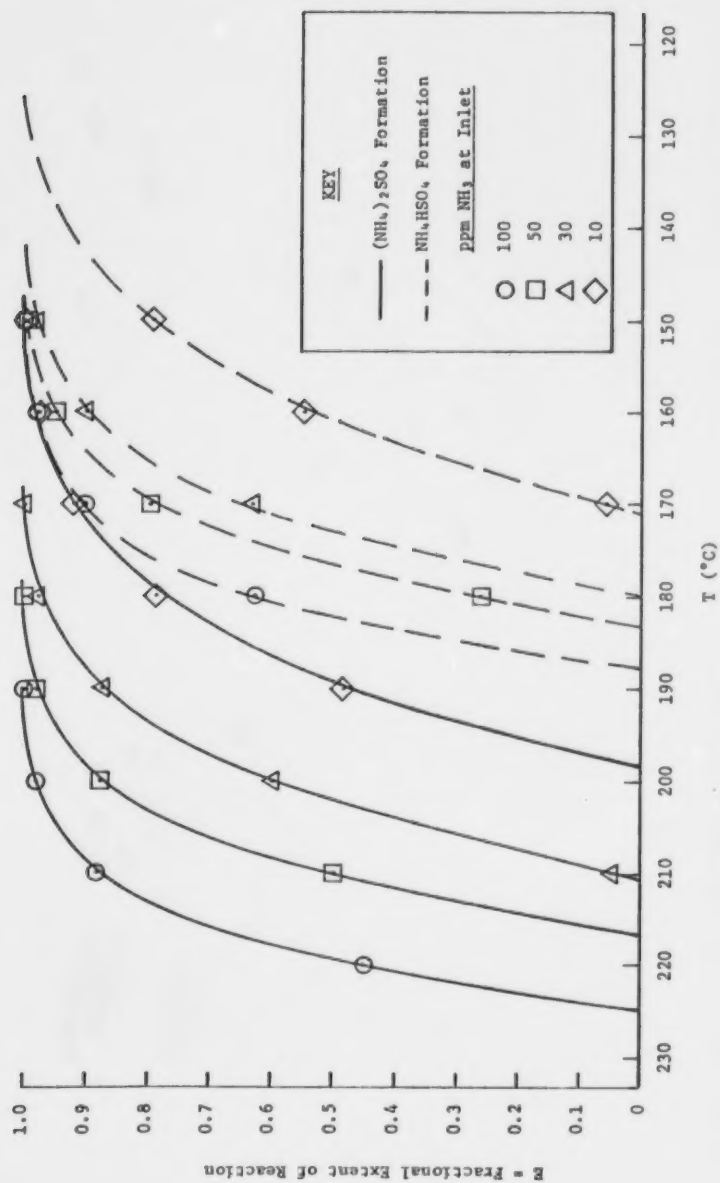


Figure 5-3. Thermodynamic equilibria for ammonium sulfate and ammonium bisulfate with 10 ppm SO_3 at inlet.

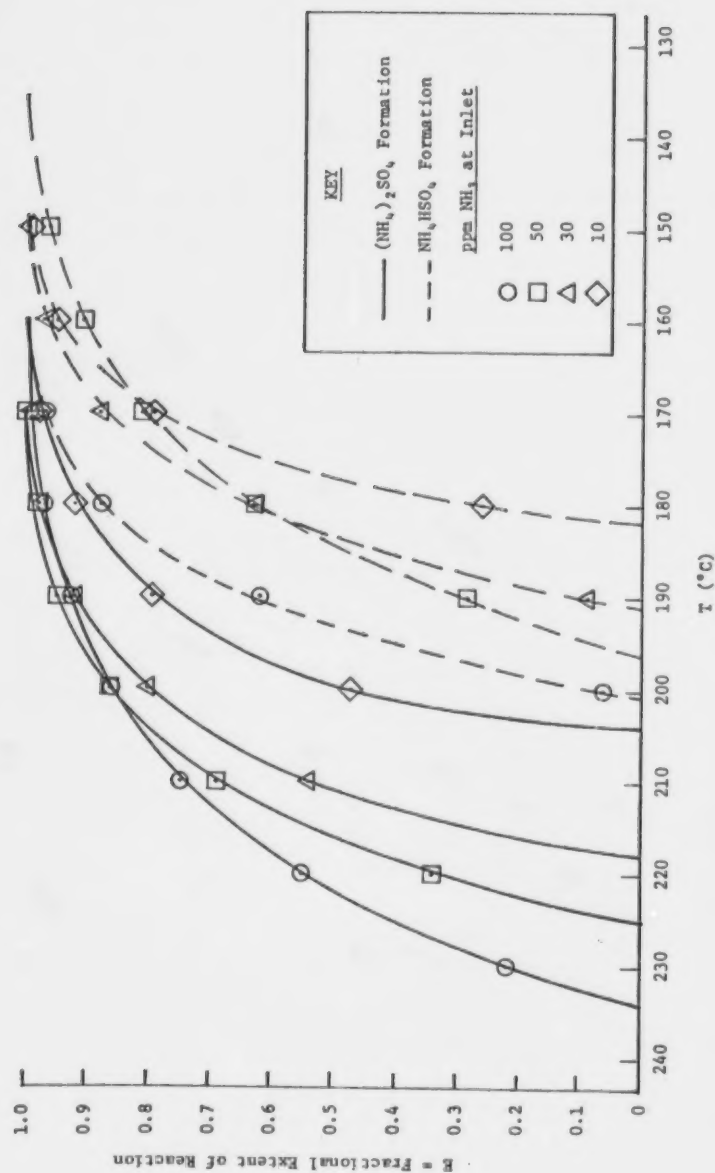


Figure 5-4. Thermodynamic equilibria for ammonium sulfate and ammonium bisulfate with 50 ppm SO₃ at inlet.

Figures 5-2, 5-3, and 5-4 are plots of the fractional extent of reaction, E, versus temperature. Fractional extent of reaction is defined here as the fraction of the stoichiometrically limiting species that can react for a given temperature and inlet NH_3/SO_3 concentrations as shown in Table 5-3.

TABLE 5-3. FRACTIONAL EXTENT OF REACTION DEFINED AS A FUNCTION OF REACTION PRODUCT AND NH_3/SO_3 MOLE RATIO

NH_3/SO_3 Ratio		E
Bisulfate Formation	Sulfate Formation	
> 1	> 2	$(Y_{\text{SO}_3}^i - Y_{\text{SO}_3}^f) / (Y_{\text{SO}_3}^i)$
< 1	< 2	$(Y_{\text{NH}_3}^i - Y_{\text{NH}_3}^f) / (Y_{\text{NH}_3}^i)$

where: i = initial, f = final and Y_a = mole fraction of species a.

As shown in Figures 5-2, 5-3, and 5-4, the initial product formation temperature increases with increasing NH_3 concentrations although the rate of increase declines. This phenomenon is shown more vividly in Figure 5-5 where the initial product formation temperature is plotted versus inlet NH_3 concentration. Examination of Equations 5-4 and 5-5 identifies the reason for this behavior.

$$K_{(\text{NH}_4)_2\text{SO}_4} = \frac{1}{(P_{\text{NH}_3})^2 (P_{\text{SO}_3}) (P_{\text{H}_2\text{O}})} \quad (5-4)$$

$$K_{\text{NH}_4\text{HSO}_4} = \frac{1}{(P_{\text{NH}_3}) (P_{\text{SO}_3}) (P_{\text{H}_2\text{O}})} \quad (5-5)$$

For constant SO_3 and H_2O concentrations, a change in NH_3 concentration will have a larger impact on the $(\text{NH}_4)_2\text{SO}_4$ equilibrium constant since the NH_3 concentration appears as a squared term. On the other hand, a change in

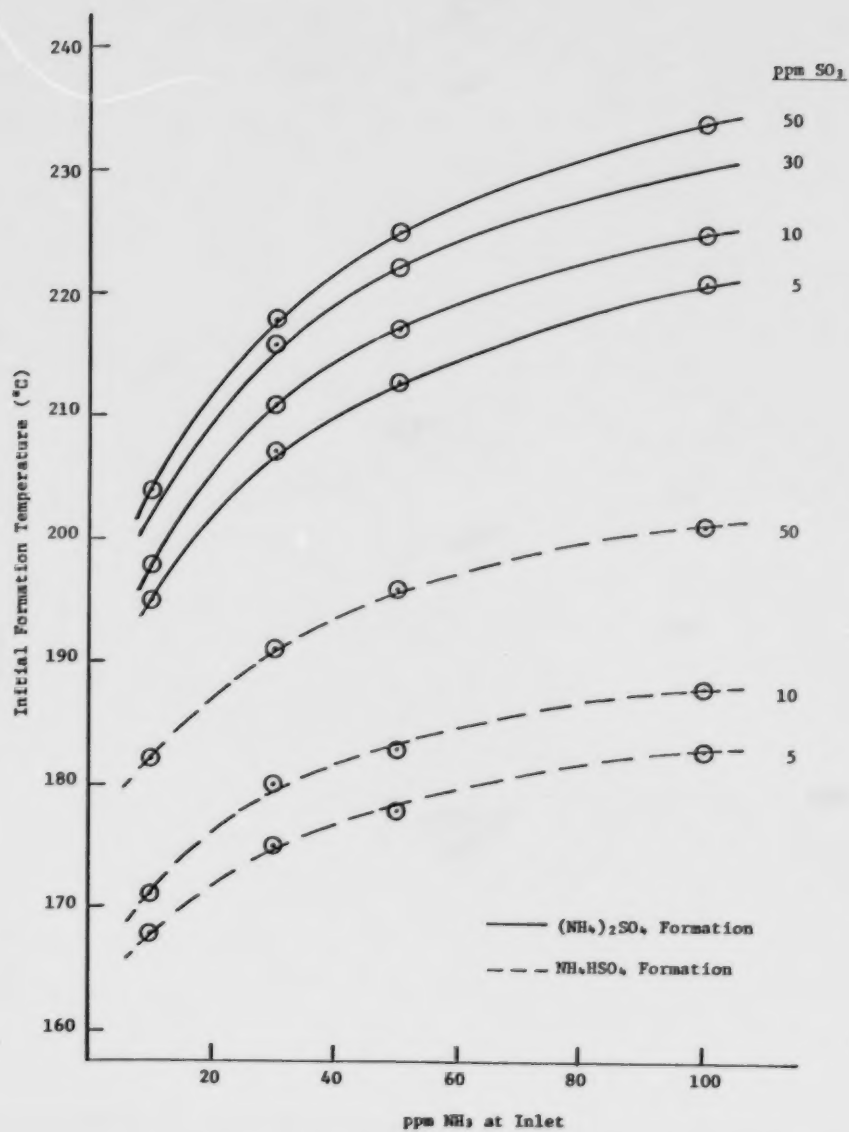


Figure 5-5. Initial product formation temperature as a function of NH₃ at inlet.

SO_3 concentration has a greater impact on the NH_4HSO_4 equilibrium constant since it represents a larger fraction of the denominator in Equation 5-5 than in Equation 5-6. Assuming that NH_4HSO_4 is the product which results in deposit formation, it appears that both the NH_3 and SO_3 concentrations should have an equal impact on the formation temperature. As shown in Figure 5-5, however, an increase in SO_3 concentrations has a slightly larger impact on formation temperature. This is due to the shift in the equilibrium between SO_3 and H_2SO_4 .

The fact that formation temperature increases with increasing concentrations is significant in terms of air preheater operation. As the formation temperature increases, the percentage of the preheater in which deposits can form and thus the extent of the deposition problem will also increase. This also indicates that the deposition problem can be reduced by reducing either the NH_3 or SO_3 concentration in the flue gas.

Another result of the thermodynamic analysis is that the formation of both $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 occurs in a narrow temperature range. The temperature drop required to permit 90 percent reaction of NH_3 and SO_3 is approximately 30°C and approximately 20°C for 80 percent reaction. This is significant in terms of air preheater operation. It means that most deposition could be limited to a small region of the preheater. While Japanese experience has not shown evidence of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition being confined to a narrow region, it may be possible to modify air preheater design so this occurs.

Another significant result of Radian's thermodynamic analysis is that the predicted formation temperatures for $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 were lower than those predicted by investigators in Japan. It appears that previous investigators' thermodynamic analyses of these reactions may have excluded the sulfuric acid formation reaction.

In the temperature range of product formation, over 90 percent of the SO_3 that was present at the inlet of the air preheater has been converted to

H₂SO₄ vapor. This tends to lower the product formation temperatures since there is effectively less SO₃ available for reaction. Also, the formation reactions involving H₂SO₄ occur at lower temperatures due to the smaller free energy change associated with these reactions. This is shown graphically in Figures 5-6 and 5-7 on the following pages. Radian's estimated initial formation temperatures are ~40°C less for ammonium bisulfate and ~20°C less for ammonium sulfate than those of other investigators. The reason the NH₄HSO₄ formation temperature is so much lower is that essentially all the SO₃ is present as H₂SO₄ in the temperature range in which NH₄HSO₄ forms. Therefore, the reaction which forms NH₄HSO₄ is that between NH₃ and H₂SO₄ which has a lower free energy change and consequently occurs at a lower temperature.

5.2 KINETIC ANALYSIS OF (NH₄)₂SO₄/NH₄HSO₄ FORMATION AND DEPOSITION

The deposition of ammonium sulfate compounds on heat transfer surfaces falls into the general classification of simultaneous heat and mass transfer problems. Deposition of NH₃ and SO₃ (or H₂SO₄ vapor) reaction products is a more complex problem than that typically treated in the literature. First, NH₃ and SO₃ (or H₂SO₄) undergo chemical reaction as opposed to condensation. Second, the compounds formed are not well defined. Several possible reaction products can be present in the deposits which form on the heat transfer surface.

The flue gas temperature downstream of an SCR process is about 400°C. The flue gas contains H₂O, SO₃, residual NH₃, and other species. As it is cooled, the SO₃ and H₂O react to form vapor phase H₂SO₄. Upon further cooling, the NH₃ and SO₃ or H₂SO₄ react to form condensate products on the heat exchanger surface and aerosol products in the bulk gas. Some of the aerosol remains in the bulk gas and some is deposited on the heat transfer surface. The primary objective of this analysis is to identify the factors which control (NH₄)₂SO₄/NH₄HSO₄ formation and deposition, and hence, to be able to predict the amount of condensate and aerosol products that form under given conditions.

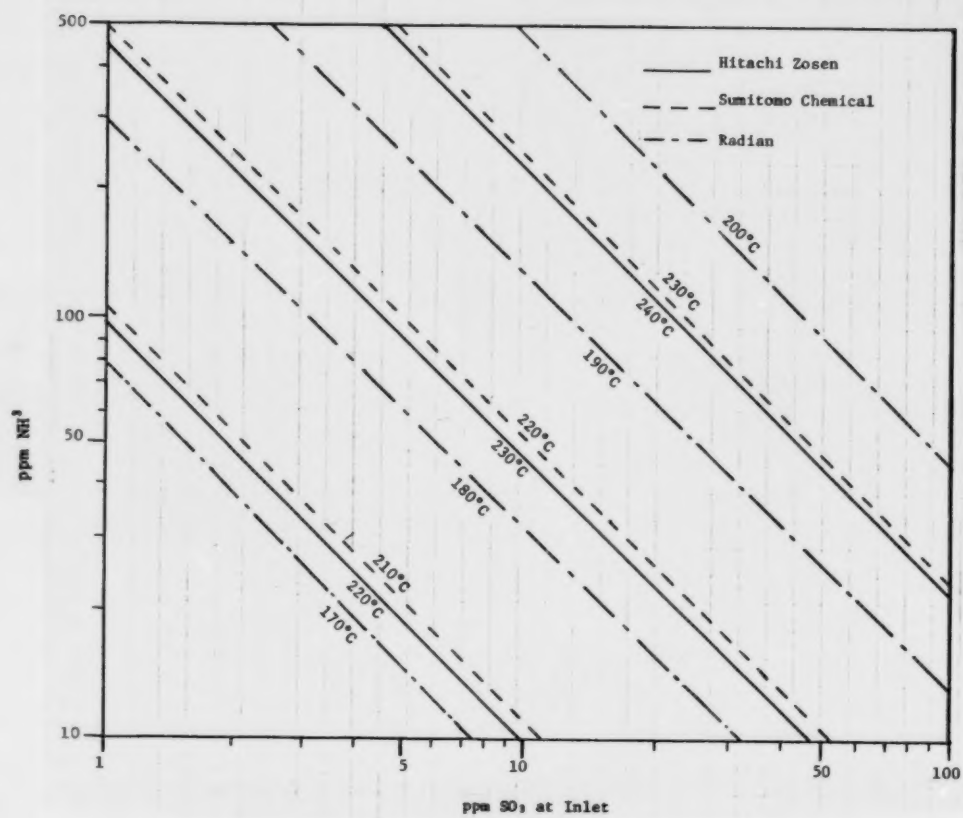


Figure 5-6. NH_4HSO_4 initial formation temperature.

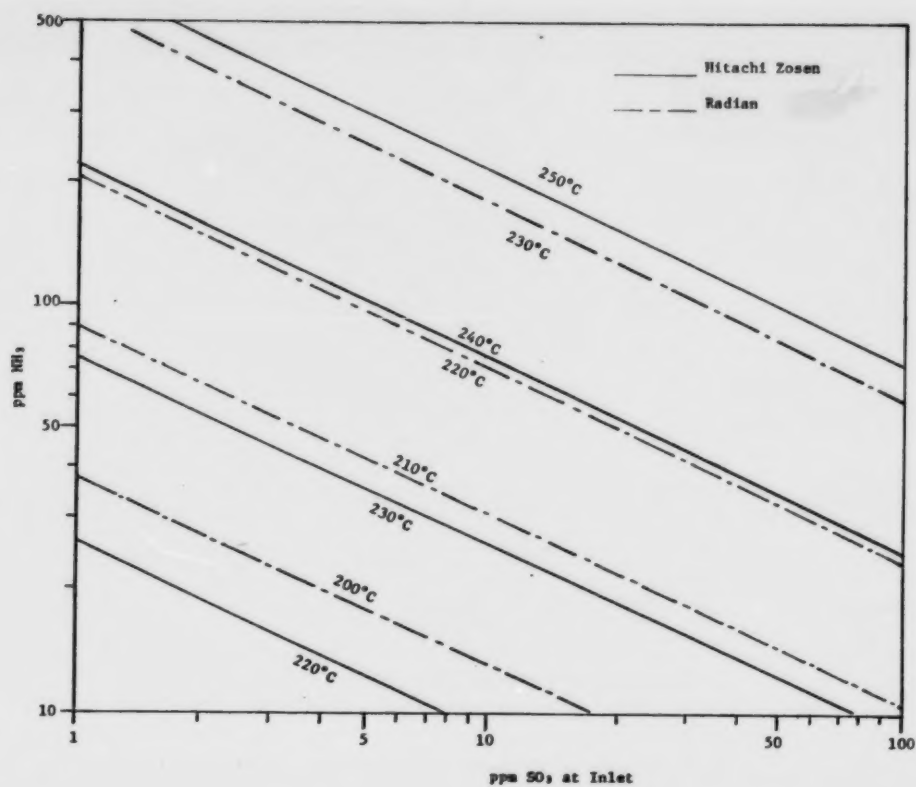


Figure 5-7. $(\text{NH}_4)_2\text{SO}_4$ initial formation temperature.

In an effort to identify the factors which control $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposit formation, a model was developed. There are basically four distinct, yet interrelated physical phenomena of importance to a model of the deposition of ammonium sulfate compounds on heat transfer surfaces. These are:

- chemical reaction thermodynamics,
- heat transfer,
- mass transfer, and
- chemical reaction kinetics.

First, thermodynamic calculations are required to estimate the temperature range in which deposits will form and to determine the driving force for mass transfer. (These calculations have been described in Section 5.1 and a more detailed description appears in Appendix A). Second, a description of the heat transfer characteristics of the system is required. Mass transfer calculations may then be made and the quantity of deposits estimated.

Several assumptions were made in addressing the need to include chemical reaction kinetics in the model. First, NH_4HSO_4 was assumed to be the only product formed in the heat exchanger. The basis for this assumption was the fact that the deposits found in an experimental system had an NH_3/SO_3 mole ratio of about 1.1. Second, the chemical reaction rate was assumed to be rapid relative to the heat and mass transfer rates. Available data indicate the chemical reaction occurs almost instantaneously at low temperatures. The validity of these assumptions will be discussed later in this section.

The impacts of heat and mass transfer on the formation and deposition of ammonium sulfate compounds are discussed next. As mentioned above, the system thermodynamics are discussed in Section 5.1 and the reaction kinetics are assumed to be quite rapid.

5.2.1 Approach

Heat Transfer--

Simultaneous heat and mass transfer are normally modeled as transport through a boundary layer (or film) between a completely mixed bulk gas and the heat transfer surface. The rapidity of heat transfer is determined by the bulk gas properties, such as thermal conductivity, and the thermal driving force.

Thermal conductivity describes the ability of a substance to conduct heat. For gases, thermal conductivity is determined primarily by movements of and collisions between molecules. This is, to a first approximation, determined by the bulk gas molecular weight.

Because the concentrations of NH_3 and SO_3 in the flue gas will not significantly change the bulk properties of the flue gas, the heat transfer rate is not affected by formation of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$. Temperature profiles in a heat exchanger may be calculated directly from the streams' inlet and outlet temperatures and the exchanger's dimensions. A simplified energy balance is given in Equation 5-7.

$$G C_p dt + q dA = 0 \quad (5-7)$$

where: G = mass flow of gas, g-moles/sec

C_p = heat capacity of gas, cal/g-mole $\cdot^\circ\text{K}$

dt = differential temperature change of gas, $^\circ\text{K}$

q = heat flux, cal/cm $^2\cdot\text{sec}$

dA = differential heat transfer surface area, cm ^{2}

The value of the heat flux, q , may be calculated from film or overall considerations.

$$\text{Film heat transfer} \quad q = h_i(t-t_i) \quad (5-8a)$$

or

$$\text{Overall heat transfer} \quad q = U(t-t_c) \quad (5-8b)$$

where: q = heat flux, $\text{cal/cm}^2 \cdot \text{sec}$

h_i = gas film heat transfer coefficient, $\text{cal/cm}^2 \cdot \text{sec} \cdot ^\circ\text{K}$

t = bulk gas temperature, $^\circ\text{K}$

t_i = interface temperature, $^\circ\text{K}$

U = overall heat transfer coefficient, $\text{cal/cm}^2 \cdot \text{sec} \cdot ^\circ\text{K}$

t_c = coolant temperature, $^\circ\text{K}$

To quantify the system's heat transfer characteristics, Equation 5-8b is written as a differential and numerically integrated over the length of the heat exchanger. (For details of this procedure, see Appendix B). Knowing h_i and U , Equations 5-7 and 5-8b are then combined to calculate the temperature change of the gas as it passes to the next area increment down the exchanger (Equation 5-9).

$$dt = \frac{-U}{GC_p}(t-t_c)dA \quad (5-9)$$

The temperature of the gas in the next area increment is equal to the sum of the gas temperature in the previous increment, t , and the temperature change, dt . Bulk gas properties are evaluated at the new temperature and then new values of h_i and U are calculated. The gas temperature change to the next area increment is then calculated and the process is repeated through the exchanger to the outlet.

Mass Transfer--

Once the heat transfer characteristics of the system have been described, the mass transfer of the gaseous components can be determined. The mass transfer rate and hence the deposition of ammonium sulfates is temperature dependent and therefore dependent on the heat transfer rate.

Mass transfer will occur in an NH_3 - SO_3 -heat exchanger system due to a concentration gradient between the bulk gas and the gas film. This concentration gradient results from reaction of NH_3 and SO_3 at the surface to form NH_4HSO_4 , thus reducing the NH_3 and SO_3 concentrations in the film. The driving force for mass transfer will be proportional to the concentration gradient which is dependent on the rate of heat transfer and the diffusivity of NH_3 and SO_3 (H_2SO_4).

The mass transfer model is complicated by the fact that the condensing material is the result of a chemical reaction. As a result, the diffusing species are not the condensing species. The diffusivity of the gaseous components is determined by the molecular motion of the diffusing species. Diffusivity, like thermal conductivity, is primarily a function of molecular weight and to some extent, a function of temperature. There is a major difference though. Thermal conductivity is based on the bulk gas properties. Diffusivity is based on properties of the individual species.

In applying the model to a heat exchanger, two cases must be considered. The first case assumes that reaction only occurs at the surface of the heat exchanger and that the bulk gas is superheated with respect to NH_4HSO_4 formation (i.e., the formation temperature of NH_4HSO_4 is below the bulk gas temperature). In the second case, reaction at the surface is considered along with simultaneous formation of NH_4HSO_4 aerosol in the bulk gas. This latter case is more representative of the actual formation/deposition phenomenon as discussed later in this section.

In order to estimate the quantity of NH_4HSO_4 which condenses on the surface and the quantity which forms as an aerosol, the bulk gas temperature and tube wall temperature must be measured or estimated. Then the stagnant film layer can be checked for saturation using the equilibrium expression derived from the thermodynamic analysis. (This expression is written in terms of the decomposition reaction for calculational convenience.)

$$K = 4.60 \times 10^{-12} \exp \left[27,280 \left(\frac{1}{423} - \frac{1}{T} \right) \right] \quad (5-10)$$

If the partial pressure product of the gaseous reactants (see Equations 5-13a and 5-13b for partial pressure products) is greater than the equilibrium constant (K value), then the mass transfer integration is begun. This involves the solution of the following equations:

Material Balance

$$F = G(y_{a,\text{inlet}} - y_a) - Gx \quad (5-11a)$$

$$F = G(y_{s,\text{inlet}} - y_s) - Gx \quad (5-11b)$$

Mass Transfer

$$Gdx = k_a P(y_a - y_{ai}) dA \quad (5-12a)$$

$$Gdx = k_s P(y_s - y_{si}) dA \quad (5-12b)$$

Equilibrium

$$K(t) = P y_a y_s \quad (5-13a)$$

$$K(t_i) = P y_{ai} y_{si} \quad (5-13b)$$

where:

- F = moles of aerosol formed, g-moles/sec
- G = moles of flue gas, g-moles/sec
- $y_{a,inlet}$ = bulk gas NH_3 concentration at exchanger inlet, ppm
- y_a = bulk gas NH_3 concentration, ppm
- x = moles of condensate per mole of flue gas
- $y_{s,inlet}$ = bulk gas SO_3 concentration at exchanger inlet, ppm
- y_s = bulk gas H_2SO_4 concentration, ppm
- dx = change in moles of condensate per mole of flue gas
- k_a = NH_3 mass transfer coefficient, g-moles/cm²·sec·atm
- P = system pressure, atm
- y_{ai} = interface (film) NH_3 concentration, ppm
- dA = differential surface area, cm²
- k_s = H_2SO_4 mass transfer coefficient, g-mole/cm²·sec·atm
- y_{si} = interface (film) H_2SO_4 concentration, ppm
- $K(t)$ = equilibrium constant at bulk gas temperature t , atm²
- $K(t_i)$ = equilibrium constant at interface (film) temperature t_i , atm²

This system requires the simultaneous solution of six equations (not all linear) with six unknowns (y_a , y_{ai} , y_s , y_{si} , F and x). If the bulk gas is superheated, $F = 0$ and the system is simplified. The solution of this system of equations involves a computer program using a double trial-and-error iterative method. Details of this work are presented in Appendix B.

5.2.2 Application of Theoretical Model to Experimental System

Dr. Ando and his associates made qualitative and quantitative tests on deposits of NH_3 - SO_3 - H_2O compounds using the apparatus shown in Figure 5-8. Gaseous SO_3 , produced by heating sulfuric acid, was mixed with preheated air and ammonia. The gas mixture was heated to 400°C in a silica tube placed

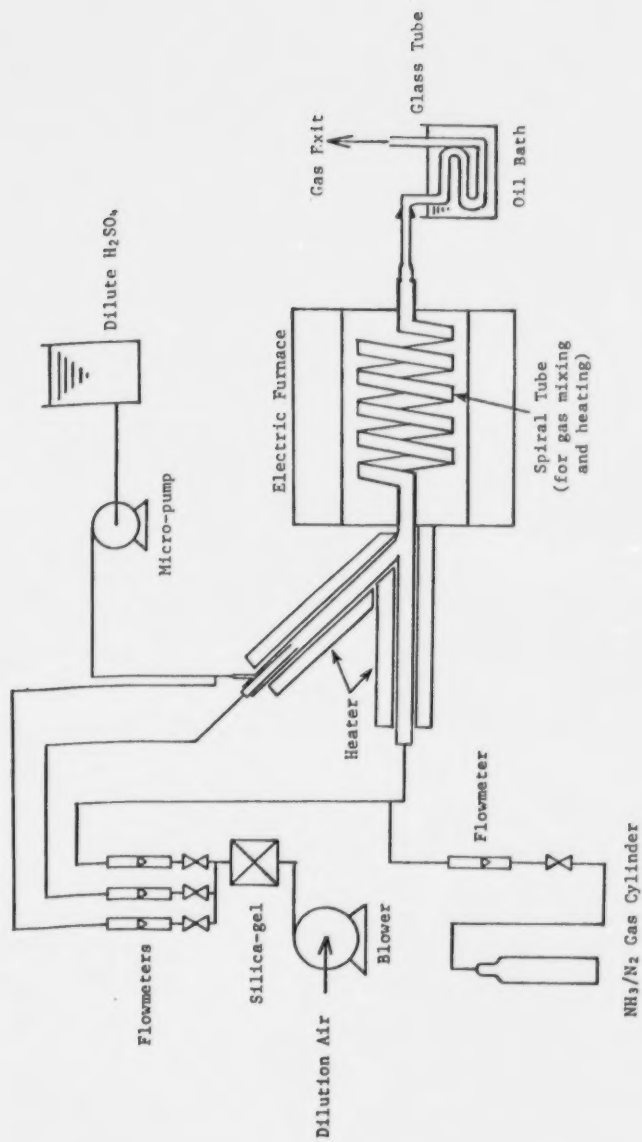


Figure 5-8. Dr. Ando's experimental apparatus.

in an electric heater. It then passed through a glass tube with an 0.95 cm ID and a length of 120 cm which was immersed in an oil bath. The bath was maintained at a desired temperature between 120 and 280°C. The glass tube consisted of 11 sections: 5 straight sections, 4 curved sections, and special entrance and exit sections. After the gas was passed through the tube for a specified time, the tube was removed from the bath. The inside of the tube (either each individual section or the whole tube, depending on the test) was washed with water to dissolve the deposits. The wash liquor was then analyzed chemically to determine the amount and composition of the deposits.

Tests were conducted with a gas rich in SO_3 and NH_3 (200 ppm each) because of the ease of the experiments. Tests with lower concentrations were also made and the results were similar to those with high concentrations. (All test gases contained 10 percent H_2O). X-ray diffraction analyses showed that for the tests with 200 ppm of both NH_3 and SO_3 , the major compound formed was NH_4HSO_4 . There were also small amounts of a double salt, $\text{NH}_4\text{HSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$, present. This suggests that, at NH_3/SO_3 ratios close to 1.0, the kinetically favored reaction product is ammonium bisulfate. This is further confirmed by Ando's tests with inlet NH_3/SO_3 mole ratios >1 ; the deposits formed at the beginning of the tube were primarily bisulfate. Recalling the results of the thermodynamic analysis, ammonium sulfate is the thermodynamically favored product. However, thermodynamics determines the temperature range for which a chemical reaction can possibly occur, not how quickly it will occur. Therefore, for the first attempts to apply the theoretical model for the formation of ammonium sulfate compounds to experimental data, ammonium bisulfate was the reaction product chosen.

The theoretical model was applied to those tests conducted by Dr. Ando in which the amount of reaction product formed was measured for each section of tube. The values for the parameters (inputs to the theoretical model)

describing those tests are shown in Table 5-4. Appendix B contains specific details of the procedure for applying the theoretical model to Dr. Ando's experiments.

TABLE 5-4. PARAMETERS FOR THEORETICAL MODEL

Test Number	Oil Bath Temperature (°C)	Gas Velocity* (Ncm/sec)	Gas Inlet T (°C)	Gas Outlet T (°C)
1	160	100	208	161
2	160	600	338	169
3	160	1000	357	174

*The gas velocity units of Ncm/sec represent the volumetric flow of gas at 0°C (Ncm³/sec) through a cross-sectional area (cm²).

5.2.3 Results and Discussion

The results of calculations using the model for tests 1, 2, and 3 are shown in Figures 5-9, 5-10, and 5-11. The figures are plots of the fractional amount of NH_3 and H_2SO_4 converted to NH_4HSO_4 in each 10 cm zone of the heat exchanger tube. The solid line in each figure is a smooth curve drawn through the data points from Dr. Ando's experimental results. The dashed lines represent the theoretical predictions from the model presented here. The lower of the two dashed lines represents only the amount of NH_4HSO_4 that actually forms at the heat transfer surface (interface) in each zone. The upper dashed line represents the sum of the condensate and aerosol that form in each zone. The exact future of an aerosol once it forms (if it deposits on the surface and, if so, where it deposits) is uncertain. This will be discussed later.

Looking at Figures 5-9, 5-10, and 5-11 (all tests at the same oil bath temperature), an interesting trend in the condensate and aerosol curves is present. First, the peak in the aerosol curve occurs later in the tube with each test. The reason for this is that as the gas velocity increases, the gas travels further down the tube in the same period of time before it is cooled below the saturation temperature and aerosol formation begins. This is quite evident as the gas in Test 1 (100 Ncm/sec), shown in Figure B-4, reaches its bulk saturation temperature very near the tube entrance. The gas in Test 2 (600 Ncm/sec) doesn't reach its bulk saturation temperature until zone 5 or 6 (50 or 60 cm) while aerosol formation doesn't begin in Test 3 (1000 Ncm/sec) until the gas reaches zone 7 or 8 (70 or 80 cm).

Another trend in Figures 5-9, 5-10, and 5-11 is that the peak in the aerosol curve is not as great with each test. Because of the delay of aerosol formation with increasing velocity, more product has a chance to form at the heat transfer surface, since the surface is cooler than the bulk gas. This is evident in the increasing amount of condensate forming at the surface and a corresponding decrease in aerosol formation, with the tests' increasing velocity. These competing mechanisms for NH_4HSO_4 formation are summarized in Table 5-5.

TABLE 5-5. AEROSOL CONTRIBUTION

	Test 1	Test 2	Test 3
Gas Velocity (Ncm/sec)	100	600	1000
Flow Description	laminar	transitional	turbulent
Condensate + Aerosol (%)	98	96	94
Condensate Only (%)	<u>11</u>	<u>62</u>	<u>66</u>
Aerosol Contribution (%)	87	34	28

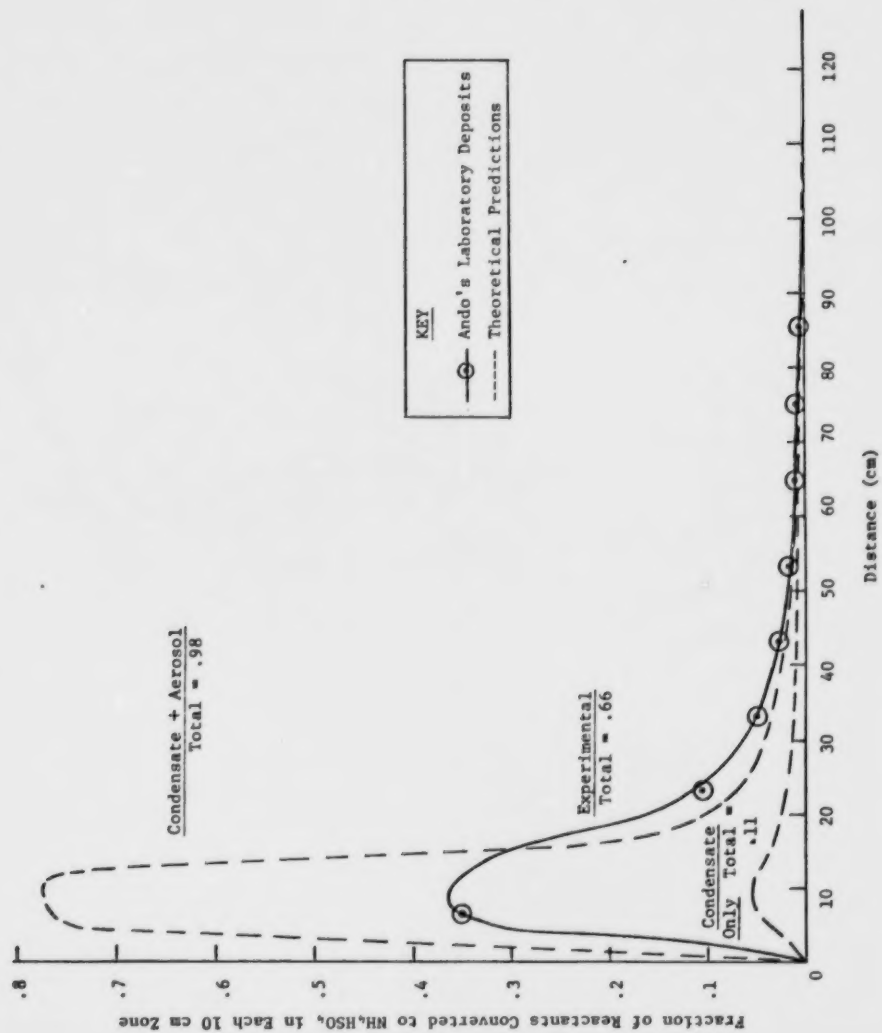


Figure 5-9. Test 1: Predicted and actual NH_4HSO_4 formation for 100 Ncm/sec gas with 200 ppm each NH_3 and SO_3 , 160°C oil bath.

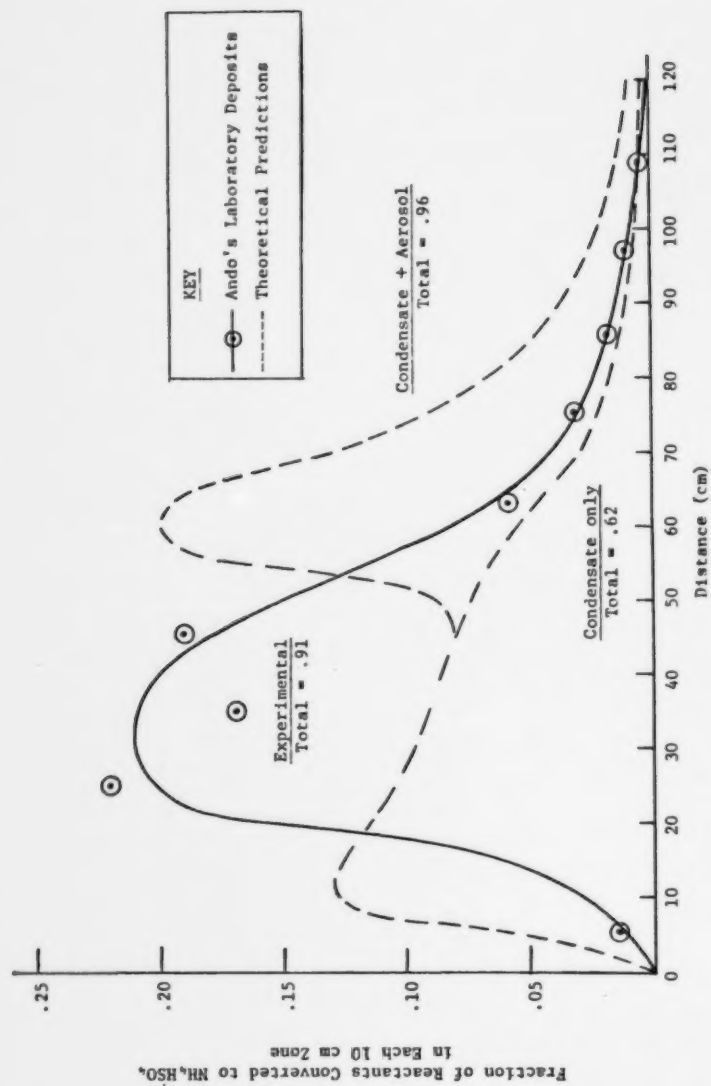


Figure 5-10. Test 2: Predicted and actual NH_4HSO_4 formation for 600 Ncm/sec gas with 200 ppm each NH_3 and SO_3 , 160°C oil bath.

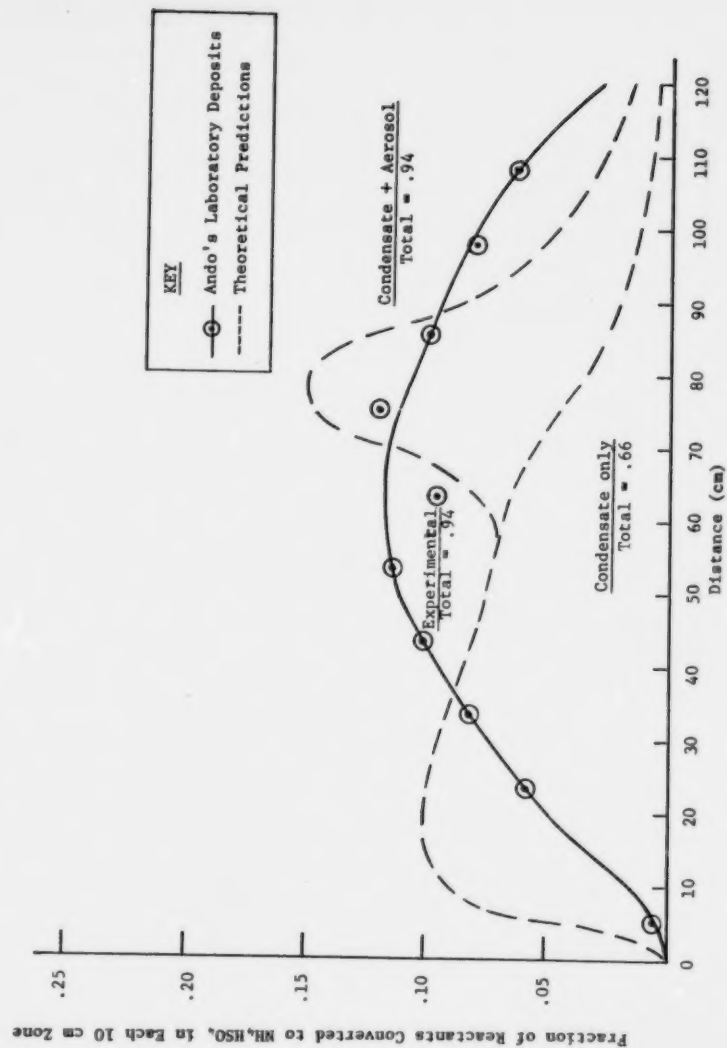


Figure 5-11. Test 3: Predicted and actual NH_4HSO_4 formation for 1000 Ncm/sec gas with 200 ppm each NH_3 and SO_3 , 160°C oil bath.

In addition to the fact that more condensate will form at increasing gas velocities, it also appears that, at higher velocities, a larger fraction of the aerosol which forms will deposit. In general, this trend agrees with results of previous work on aerosol deposition in tubes. Under laminar flow conditions, aerosol particles are deposited on the inner wall of a tube by diffusion of submicron size particles and by gravitational settling of micron size particles. For turbulent flow, the deposition is due to eddy (aggregate as opposed to molecular) diffusion. Aerosol particles deposit when they impinge on and adhere to the wall. As the gas velocity increases, the random movement of the aerosol particles is significantly enhanced and the probability of the aerosol particles impinging on the wall is also increased. Verification of this predicted trend can only be obtained through further studies. There are a number of other factors that must be identified including particle size, particle density, particle settling velocity, pipe or plate surface roughness, equipment geometry, etc.

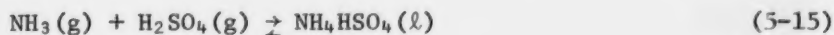
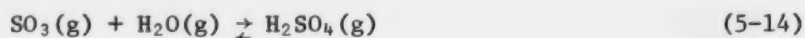
The results of the model's predictions presented in Figures 5-9, 5-10, and 5-11 are similar to those obtained in the laboratory experiments. Tests 2 and 3 show a second peak in Ando's data points that correspond to the predicted aerosol formation. The experimental points could be due to the onset of aerosol formation or to unique apparatus geometry. This indicates that the application of basic chemical engineering principles can approximate the chemical and physical phenomena of the $\text{NH}_3/\text{H}_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ system. However, the work presented here is an initial attempt at describing one experimental situation. The problem of applying this model to air preheater systems is not trivial. With detailed process data and pilot studies of the NH_4HSO_4 /air preheater system (particularly in the area of aerosol formation/deposition), the phenomena can be described precisely.

The modeling results have several implications in terms of an air preheater system. For Ando's laboratory tests the assumptions made in developing the model appear to be valid. At an initial NH_3/SO_3 mole ratio of 1.0, the principal reaction product appears to be NH_4HSO_4 and the reaction which forms

this product is very rapid. The fact that NH_4HSO_4 is the principal product formed is in apparent conflict with the thermodynamic predictions which indicate that $(\text{NH}_4)_2\text{SO}_4$ should be the only compound which forms, regardless of the initial NH_3/SO_3 stoichiometric ratio.

Apparently, the reaction which forms $(\text{NH}_4)_2\text{SO}_4$ directly from gas phase reactants is slow relative to both the rate at which the gas is cooled from the sulfate to the bisulfate formation temperature and the rate of the reaction which produces NH_4HSO_4 . As a consequence, the gas is cooled below both the $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 formation temperatures before appreciable quantities of $(\text{NH}_4)_2\text{SO}_4$ can form. At this point, the formation of NH_4HSO_4 predominates due to its more rapid reaction rate. This is not to imply that no $(\text{NH}_4)_2\text{SO}_4$ will form in a preheater. On the contrary, significant quantities of $(\text{NH}_4)_2\text{SO}_4$ will form in the presence of excess NH_3 .

In experiments using the laboratory apparatus described previously, Dr. Ando found that the composition of deposits are related to the stoichiometric ratio of the reactants. These results are summarized in Figure 5-12. Based on Ando's data and the results of the modeling work, it appears that the formation of ammonium sulfates proceeds via the reaction path shown in the following equations:



Sulfuric acid vapor is the first product formed and this reaction is essentially complete at the NH_4HSO_4 formation temperature. NH_3 then reacts with H_2SO_4 to form liquid NH_4HSO_4 which can further react with NH_3 as shown in Equation 5-16. The compound shown on the right side of Equation 5-16 represents a liquid solution of NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$. As the quantity of

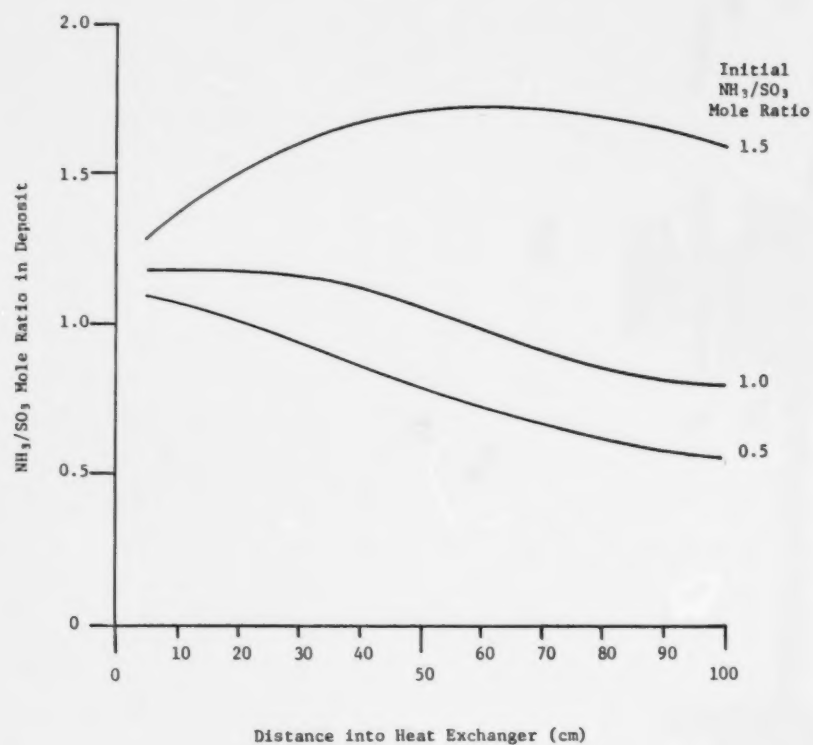


Figure 5-12. Deposit composition as a function of initial NH_3/SO_3 mole ratio and position in a heat exchanger.

excess NH_3 increases, solid $(\text{NH}_4)_2\text{SO}_4$ will form in equilibrium with the solution and if enough NH_3 is present, the deposit will contain only solid $(\text{NH}_4)_2\text{SO}_4$.

Based on available data, the NH_3/SO_3 ratio at which $(\text{NH}_4)_2\text{SO}_4$ is the only product cannot be determined. In examining Figure 5-12, it might appear that this could occur at NH_3/SO_3 ratios less than 2.0. However, Dr. Ando did not report the quantity of deposits as a function of distance in the experimental heat exchanger, so an overall deposit composition cannot be determined and no conclusions can be drawn based on his data. There is, however, evidence to indicate that large excess NH_3 levels produce deposits which contain essentially all $(\text{NH}_4)_2\text{SO}_4$.

In summary, the primary factors controlling NH_4HSO_4 and subsequent $(\text{NH}_4)_2\text{SO}_4$ formation are the concentrations of the gaseous reactants and the system temperatures. For given reactant concentrations, there is a specific temperature above which NH_4HSO_4 will not form. The question of NH_4HSO_4 deposition is more complex. The relative rates of heat and mass transfer must be considered to predict the amount of deposits. If the gas is cooled rapidly, significant amounts of NH_4HSO_4 aerosol will form in the bulk gas. Depending on system parameters (gas velocity, gas passing area, particle characteristics, etc.), some of the aerosol formed should pass through the preheater. To make accurate estimates of the amount of ammonium sulfates which form and deposit in an air preheater, detailed analysis of air preheater design and operation along with development of more fundamental data on NH_3 - SO_3 reactions are needed.

5.3 FACTORS WHICH INFLUENCE $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ DEPOSITION IN PREHEATERS

The formation and deposition of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ in an air preheater is a complex phenomenon and difficult to define. The results of the thermodynamic and kinetic analyses have identified the principal physical and chemical factors which influence deposit formation. These factors include the concentrations of NH_3 and SO_3 in the flue gas, the metal-temperatures

in the air preheater, the heat transfer rate, and the flue gas velocity. In order to estimate the extent of a deposition problem, the influence of each of these factors must be quantified.

The thermodynamic analysis presented in Section 5.1 identifies the temperature range in which the formation reactions can proceed for any given combination of inlet NH_3 and SO_3 concentrations. The results indicate that $(\text{NH}_4)_2\text{SO}_4$ is the thermodynamically favored reaction product and it can form at a higher temperature than NH_4HSO_4 . For most flue gas NH_3 and SO_3 concentrations that might be encountered in a preheater downstream of an SCR system, ammonium sulfate can form at temperatures below 230°C , while ammonium bisulfate forms at temperatures less than 200°C . Whenever the heat transfer element temperature is below the formation temperature (typically, in the intermediate temperature zone), deposit formation on the surface is possible. Aerosol formation can occur a slight distance further toward the cold-end when the bulk gas temperature is cooled below the formation temperature. The deposition of aerosols is a complex phenomenon but it appears that aerosol deposits increase under turbulent flow conditions.

The locations and severity of the deposits depends both on the NH_3 and SO_3 concentrations and the temperature profile in the preheater. As the reactant concentrations increase, deposits can form in a larger portion of the preheater, and obviously, in larger amounts. If the metal temperature is decreased, deposit formation will begin further upstream in the preheater. The seriousness of the deposition problem for given reactant concentrations, can be qualified by the temperature difference between the bisulfate formation temperature and the cold-end metal temperature. The larger the temperature difference, the more serious the problem.

The thermodynamic analysis predicts the temperatures at which reactions can proceed, but it does not indicate the rate at which they occur. In fact, the thermodynamic analysis indicates that ammonium sulfate is the favored reaction product but, laboratory experiments and analysis of air preheater

deposits have shown ammonium bisulfate to be the initial reaction product. The formation of the sulfate evidently occurs more slowly than the formation of bisulfate.

This observation is further verified by the application of the kinetic model to Dr. Ando's laboratory experiments. Two assumptions made in the development of that model were that ammonium bisulfate is the principal product and the rate of chemical reaction is very fast compared to the rate of mass or heat transfer. These assumptions appear to be valid for an NH_3/SO_3 mole ratio of 1.0. The amount and location of deposits predicted by the theoretical model agree quite well with the experimental results.

The results of the kinetic model indicate that as the gaseous reactants diffuse to the heat transfer surface in large enough quantities to saturate the film, deposits will form. Sulfates can also form in the bulk gas as aerosols. The amount of aerosol formation is controlled by the respective rates of heat and mass transfer. If the gas is cooled very quickly to its saturation temperature, before large amounts of the reactants can diffuse to the heat transfer surface and form deposits there, then significant amounts of aerosol will form. Whether an aerosol will deposit on the metal surface is dependent on the gas velocity, particle size, particle density, surface roughness, equipment geometry and other factors. Comparison of the model's results with laboratory data suggests that aerosol deposition increases with gas velocity or turbulence.

Unfortunately, the results of the thermodynamic and kinetic analyses cannot be applied directly to the data available on air preheater plugging. The reason for this is that the available data are not complete enough to permit modeling the air preheater. In general, only inlet concentrations of NH_3 and SO_3 and inlet and outlet flue gas temperatures are known. In order to quantitatively apply the results of the thermodynamic and kinetic analysis, flue gas and heat transfer element temperature profiles are required. This includes axial profiles through the preheater and angular profiles which

describe the temperature at a given depth as the preheater wheel is rotated. In addition, details of the heat exchanger geometry are required to permit calculations of gas velocity through the preheater.

Although the results of the thermodynamic and kinetic analyses cannot be quantitatively applied to air preheater operating data, a semi-quantitative analyses of these data can be conducted. The principal factors which control deposit formation in an air preheater include the concentration of reactants, the product formed, the relative flue gas and heat transfer element temperatures, and the flue gas velocity. The results of the kinetic analysis indicate that NH_4HSO_4 is the first reaction product which forms under typical preheater conditions. Subsequently, this compound can react with NH_3 to form $(\text{NH}_4)_2\text{SO}_4$. Assuming most preheaters have similar flue gas velocities, the principal factors which control deposit formation will be the temperature of the flue gas and heat transfer elements and the concentrations of reactants.

In an effort to quantify the severity of deposit formation based on the factors which control formation, a "deposition number" was developed. This number is the product of the NH_3 and SO_3 concentrations and the difference between the NH_4HSO_4 formation temperature and a representative exit temperature from the preheater as shown in Equation 5-17.

$$[\text{NH}_3] \times [\text{SO}_3] \times [T_{\text{NH}_4\text{HSO}_4} - T_{\text{rep}}] = \text{deposition number} \quad (5-17)$$

The magnitude of this number should correspond to the severity of the deposition problem (i.e., the larger the deposition number, the greater the problem). Negative numbers correspond to situations where the maximum cold-end metal temperature in the air preheater is greater than the NH_4HSO_4 formation temperature. In this case, no deposition problem would be expected.

The representative exit temperature used in Equation 5-17 is a weighted average of the cold-end metal temperature and the flue gas temperature leaving the preheater. Both these temperatures are considered important since deposits

can either form on the heat transfer surface or result from deposition of aerosols formed in the bulk gas. But because the contribution of these two effects to the overall quantity of deposits is not equal, a weighted average was developed based on the modeling results presented in Section 5.2. The modeling results indicated that, in both the transitional and turbulent flow regions, the contribution of the aerosol fraction to total deposition was about 30 percent. Using this as a basis, the representative exit temperature is defined by Equation 5-18.

$$T_{rep} = (.7)(T_{cold-end}) + (.3)(T_{exit-gas}) \quad (5-18)$$

Table 5-5 presents the deposition number for the installations discussed in Section 4 which had reported the data necessary to calculate this number. The deposition numbers are compared to the severities from Tables 4-1 and 4-8. As shown, deposition numbers below 10,000 correspond to installations which report only minor problems while numbers above 30,000 correspond to severe deposition problems. It also appears that deposition numbers between 10,000 and 30,000 correspond to moderate problems. In one case, the deposition number is negative and no problems have been reported. One exception to the general trend exhibited by the deposition numbers is the Kudamatsu station of Chugoku Electric which has encountered severe plugging problems although conditions do not indicate a severe problem would be expected. Obviously, the deposition number presented here does not account for all the factors which can influence $(NH_4)_2SO_4/NH_4HSO_4$ deposition and it should be used with caution and only as a general indicator of the potential for a deposition problem to occur.

TABLE 5-6. DEPOSITION NUMBER AND RELATIVE SEVERITY OF DEPOSIT FORMATION FOR SELECTED INSTALLATIONS

Plant	Cold-End ¹ Metal Temperature (°C)	Flue Gas Exit Temperature (°C)	Representative ² Exit Temperature (°C)	NH ₄ HSO ₄ Formation Temperature (°C)	NH ₃ (ppm)	SO ₂ (ppm)	Relative Severity of Deposition	Deposition ³ Number
Shindaiyowa Petrochemical	97	163	117	179-182	10	30-40	Moderate- Severe	26,000
Kurabo	125	220	154	173-182	3-10	40	Minor	11,200
Nippon Yakin	130-163	270-300	186	177-182	10-20	20-30	None	- 2,400
EPDC - Takasago	80-90	130-150	95	164-188	50	1-20	Severe	93,000
Kawasaki Steel	95-105	160-180	115	161	10	2	Minor	920
Nakayama Steel	105-125	180-220	128	167-172	5	10-20	Minor	4,400
Bankside Generating Station	90	150	108	177	30	7	Moderate	14,490
T/A Widows Creek No. 7	80	130	95	183	15	30	Severe	39,600
Chugoku Electric Kudamatsu	85	140	102	160	4	4	Severe	940

¹The cold-end metal temperature in an air heater is approximated by the average of the flue gas exit temperature and the air temperature entering the pre-heater. The air temperature was assumed to be 30°C.

²The representative exit temperature was calculated using the lowest values for the cold-end metal temperature and the flue gas exit temperature.

³The deposition number was calculated using the NH₄HSO₄ formation temperature and NH₃ and SO₂ concentrations which result in the highest value.

SECTION 6

POTENTIAL SOLUTIONS TO THE $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ DEPOSITION PROBLEM

The deposition of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ in air preheaters does cause operating problems. In particular, experience indicates that corrosion and plugging of the preheater can occur. However, it appears that deposition will not adversely impact the thermal efficiency of the preheater. Also, there do not appear to be any significant environmental problems associated with treatment of air preheater wash water contaminated by $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ and their corrosion products (i.e., $\text{NH}_4\text{-Fe-SO}_4$ compounds).

The overall objective of the study was to define the deposition problem and to identify and evaluate potential solutions. To meet this objective, thermodynamic and kinetic analyses were conducted. Using the results of these analyses as a basis, potential solutions to the problem have been identified. This section presents solutions to the deposition problem and provides an evaluation of the factors which must be considered in implementing these solutions.

Solutions to the $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition problem should minimize or eliminate the operational impacts of deposition (i.e., plugging and corrosion of the air preheater). This can be done in two ways: (1) modification of air preheater design and/or operation and (2) modification of SCR system design and/or operation. The following discussion presents specific techniques for minimizing the problem including a brief description of how the solutions work. A more detailed discussion of these solutions is presented in Sections 6.1 and 6.2.

Modification of Air Preheater Design/Operation

As a result of the analysis of deposit formation and air preheater operation, five possible solutions to the deposition problem have been identified. Four of the solutions require modification of the design or operation of an air preheater. The first makes use of available design options to minimize preheater operating and maintenance problems and the second solution incorporates a relatively minor design modification which can minimize plugging problems. The third solution specifies a major change in air preheater design which will eliminate deposit formation and potentially improve boiler efficiency. The fourth technique requires a modification of air preheater operation which will eliminate deposit formation but also result in a decrease in boiler efficiency.

The results of the thermodynamic and kinetic analyses indicate that NH_4HSO_4 will begin to deposit in the intermediate temperature region of an air preheater. This is the principal reason for the plugging and corrosion of the preheater. Standard preheater designs do not incorporate corrosion resistant material in the intermediate temperature zone of the preheater. Also, available soot blowing equipment is most effective in removing deposits from the ends of the preheater and not the center.

One technique for minimizing the deposition problem is to make use of available air preheater design options. This includes use of corrosion resistant material in the portion of the preheater in which deposits can form, installation of equipment to permit in-service water washing, use of combined intermediate and low-temperature zone heat transfer elements to make soot blowing more effective and use of high-pressure, hot- and cold-end soot blowers. These options should help minimize the impact of deposit formation although they do not represent preventative measures.

A second technique which can also minimize the impact of deposit formation is "heat cleaning" of the preheater. Heat cleaning involves periodically increasing the cold-end metal temperature of the preheater above the $(\text{NH}_4)_2\text{SO}_4$

formation temperature. During a cleaning period, any $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 deposits in the preheater will decompose and be carried downstream in the flue gas. However, corrosion products and fly ash deposits which have accumulated may not be removed.

A third technique recirculates flue gas from downstream of the air preheater to cool hot flue gas in a reaction chamber. The flow of the recirculated gas is adjusted so the flue gas temperature in the reaction chamber is reduced below the $(\text{NH}_4)_2\text{SO}_4$ formation temperature but not below NH_4HSO_4 formation temperature. This will result in formation of solid $(\text{NH}_4)_2\text{SO}_4$ aerosol which can pass through the preheater and be collected in an ESP.

Use of flue gas recirculation can also improve boiler efficiency. Formation of $(\text{NH}_4)_2\text{SO}_4$ will remove SO_3 from the flue gas and potentially eliminate H_2SO_4 condensation in the preheater or downstream equipment. This can permit the preheater to operate with a lower cold-end metal temperature and therefore improved boiler efficiency.

A fourth technique which can eliminate deposit formation involves raising the cold-end metal temperature in the air preheater above the NH_4HSO_4 formation temperature. The feasibility of this solution has been demonstrated by operating experience (Section 4). However, use of this technique results in a significant decrease in the thermal efficiency of the boiler.

Modification of SCR System Design/Operation

Evaluation of the thermodynamics and kinetics of deposit formation indicate that the three principal factors which control formation in a regenerative preheater are the NH_3 and SO_3 concentrations in the gas and the operating temperatures in the preheater. In addition, operating experience indicates that in most cases, NH_3 emissions below 10 ppm will minimize deposit formation. Modification of the design and operation of the SCR system can be used to reduce the flue gas NH_3 concentration and thereby minimize deposit

formation. The principal modifications which can be employed to lower NH_3 emissions are an increase in the quantity of catalyst with a simultaneous decrease in the NH_3 injection rate.

There are several factors which determine the NO_x reduction efficiency of an SCR system. These include the stoichiometric ratio of NH_3 injected to NO_x in the flue gas (NH_3/NO_x mole ratio) and the quantity of catalyst in the reactor. These two factors can be varied simultaneously (within limits) while maintaining constant NO_x reduction efficiency. In other words, a trade-off exists between the quantity of catalyst used and the amount of NH_3 injected into the reactor.

In order to achieve a specified NO_x removal efficiency with a minimum of NH_3 emissions, the NH_3/NO_x mole ratio should be minimized resulting in the requirement for a relatively large quantity of catalyst. For example, if 90 percent NO_x reduction is required, the theoretical minimum NH_3/NO_x mole ratio is approximately 0.9 (in practice, this ratio must be higher since some NH_3 will be oxidized by the catalyst). For this minimum NH_3/NO_x ratio, the quantity of catalyst required to achieve 90 percent NO_x reduction could be determined and the resulting system design would minimize NH_3 emissions from the process.

In practice, minimization of NH_3 emissions would require that both the NH_3 injection rate and the quantity of catalyst be varied. The limits for each parameter would be determined by design constraints including required NO_x removal efficiency and acceptable NH_3 emission levels.

Basis for Assessment

In order to assess the feasibility of each of the potential solutions which have been identified, a basis was developed. This basis is a model

boiler-SCR-Air Preheater system with the characteristics shown in Table 6-1. An evaluation was conducted for each of the potential solutions to the deposition problem using the model system as a base case. The objective of this evaluation was to determine the requirements for minimizing or eliminating deposit formation. In the case of SCR operation, changes were made to reduce NH_3 emissions to several levels. Where applicable, heat and material balances were completed. Finally a rough cost estimate was developed for each option. This cost estimate is based on a new installation and not a retrofit. It is expected that retrofit costs can be significantly higher.

Sections 6.1 and 6.2 present a more complete discussion of the potential solutions to the deposition problem including an evaluation of the technical feasibility. In addition, the results of an economic analysis are presented.

6.1 MODIFICATION OF AIR PREHEATER DESIGN/OPERATION

Four methods of minimizing or eliminating $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition problems which involve modification of preheater design and/or operation have been identified. They are:

- Use of Available Design Options
- Heat Cleaning of Deposits
- Flue Gas Recirculation
- Increase Air Preheater Cold-End Metal Temperature

Each of these methods should reduce or eliminate the deposition problem. In addition, each method will change the capital and/or operating costs of the air preheater.

TABLE 6-1. BASIS FOR BOILER-SCR-AIR PREHEATER EVALUATION

Parameter	Base Value
<u>Boiler Characteristics</u>	
• Size	500 MWe
• Thermal Efficiency	88%
• Number of Air Preheaters	2
• Flue Gas Flowrate	620 kg/sec (82,000 lb min)
• Heat Rate	9000 Btu/kWh
<u>Flue Gas Characteristics</u>	
• Reactor Inlet	
--NO _x concentration	350 ppm
--NH ₃ concentration	350 ppm
--SO ₃ concentration	10 ppm
--temperature	350°C
• Reactor Outlet	
--NO _x concentration	35 ppm
--NH ₃ concentration	30 ppm
--SO ₃ concentration	10 ppm
• Air Preheater Outlet	
--NO _x concentration	35 ppm
--NH ₃ concentration	20 ppm
--SO ₃ concentration	0 ppm
--NH ₄ HSO ₄ concentration	10 ppm equivalent
--temperature	150°C
<u>SCR Characteristics</u>	
• Relative Quantity of Catalyst	1.0
• NO _x Removal Efficiency	90%
• NH ₃ /NO _x Mole Ratio	1.0
<u>Air Preheater Characteristics</u>	
• Type/Size	Ljungstrom Tri-Sector/Size 31
• Number of Soot Blowers	1 per air preheater (cold-end)
• Soot Blowing Frequency	3 times per day
• Soot Blowing Steam Pressure	1.48 MPa (200 psig)

The following discussion presents an evaluation of each of the four solutions which involve modification of air preheater design/operation. The estimated energy consumption for each solution is based on the data gathered during this study. The costs of each modification are rough estimates and intended to provide a relative ranking of each method. The degree of deposit reduction is based strictly on technical evaluation. Little or no operating experience is available to support this work.

6.1.1 Use of Available Design Options

One method of limiting the impact of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposit formation is to make use of available options when specifying an air preheater design. Specifically, this includes:

- both hot- and cold-end soot blowers,
- increased soot blowing frequency,
- increased soot blowing steam pressure,
- provisions for in-service water washing of the preheater,
- use of corrosion resistant material in the intermediate and low temperature zones of the preheater, and
- use of combined intermediate and low temperature heat transfer elements.

Most of these options will increase the annualized costs of air preheater operation. However, the effect of employing the options should minimize any impact associated with $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition. Use of combined heat transfer elements, increased soot blowing intensity, and in-service washing should prevent forced boiler outages due to plugging of the preheater. The use of corrosion resistant material in the preheater should permit reliable air preheater operation over the life of the unit.

Each of the options will require some change in air preheater design or operation. Unfortunately, very little experience is available and the required changes in design/operation are difficult to quantify. Any estimates made must be based largely on engineering judgment. However, there is evidence which indicates that the heat transfer element and soot blowing modifications recommended in this section will work. EPDC has recently awarded a contract for two Ljungstrom type heat exchangers to be installed downstream of a de-NO_x system. These preheaters will have combined intermediate and low temperature zone heat transfer elements made of corrosion resistant material. The soot blowing equipment/operation specified for these preheaters includes 3 soot blowers on both the hot- and cold-end (gas side) of the preheater. Steam pressure for soot blowing is 1.48 mPa (200 psig) at the hot-end and 1.69 mPa (230 psig) at the cold-end. Specified soot blowing frequency is once every 4 hours on the cold-side and every 12 hours on the hot-side. According to Gadelius, the air preheater manufacturer, tests indicate that the soot blowing equipment specified provides effective cleaning of NH₄HSO₄ deposits and the pressure drop through the preheater remains relatively constant.²²

The following discussion examines each of the design options which are recommended and estimates the change associated with those options including quantification of energy consumption and capital costs.

Hot and Cold End Soot Blowers

Most air preheater designs for coal and oil fired power plants have soot blowers located at the cold-end of the preheater on the gas side. In applications with low-rank fuels (e.g., lignite), soot blowers are also located at the high temperature end of the preheater to prevent fouling of heat transfer elements.⁶ For this evaluation, the base case assumes a single cold-end soot blower per preheater.

In order to help minimize deposit build-up in the air preheater, hot-end soot blowers should be employed. This will supplement the cold-end soot blowers while adding only marginally to the capital cost of the preheater. It will also increase the operating costs for the air preheater by increasing the steam requirements for soot blowing. This modification appears to be effective in controlling deposits when used in conjunction with the use of combined heat transfer elements. No full scale operating data are available but, the results of EPDC's pilot tests indicate that these modifications will help minimize deposit build-up.

For this evaluation, soot blowers will be added to both the hot- and cold-end of the preheaters. These modifications will result in a total of six soot blowers per preheater which is equivalent to the design specified by EPDC. This should help minimize $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition in the air preheaters.

Use of Combined Heat Transfer Elements

Japanese experience has shown that $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposits tend to accumulate at the interface between the intermediate and low temperature heat transfer elements in a preheater. In order to minimize deposition in this location, EPDC and Gadelius have developed a preheater with combined intermediate and low temperature heat transfer elements. This arrangement along with a conventional preheater design is shown schematically in Figure 6-1. The use of the modified air preheater design also has the added benefit of making the cold-end soot blowers more effective in the intermediate temperature zone.

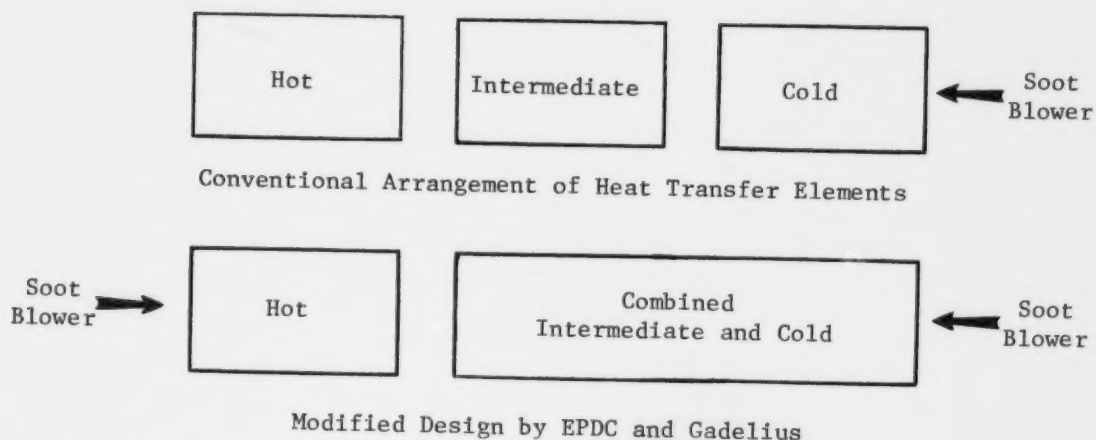


Figure 6-1. Comparison of conventional and modified air preheater designs.

Increased Soot Blowing Frequency

A change in air preheater operation which may reduce deposit build-up is an increase in soot blowing frequency. This will also result in an increase in air preheater operating costs. The model air preheater system has a soot blowing frequency of 8 hours. For this evaluation, the frequency will be doubled to once every 4 hours which doubles the quantity of steam required for soot blowing. The increased steam consumption is quantified in the heat balance presented later in this section. This frequency was selected based on the information available from EPDC.

Increased Soot Blowing Steam Pressure

A third change which can reduce deposit build-up is an increase in the steam pressure used for soot blowing. The general procedure for determining the operating pressure is to start at 1.48 MPa (200 psig) and increase it until soot blowing becomes effective. For the base case, a pressure of 1.48 MPa (200 psig) was assumed. This evaluation specifies 1.82 MPa (250 psig)

which is the maximum operating pressure for conventional soot blowing equipment. This change results in a slight increase in the energy consumed during soot blowing since higher pressure steam contains more energy per unit weight. In addition, increasing the steam pressure can cause accelerated wear of the heat transfer elements and is not generally recommended by the manufacturer.

Data on the effectiveness of increased steam pressure is not available. Some of the experience reported in Section 4 indicates that "stronger" soot blowing has had limited success in controlling deposit formation. However, the information from EPDC does not indicate that unusually high pressure steam will be used in their preheater design, possibly due to the detrimental impact of high pressure steam. Obviously, test data are required to quantify the effect of increased soot blowing pressure and other modifications to soot blowing design/operation.

Provisions for In-Service Water Washing of the Preheater

Evidence indicates that $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition in an air preheater can present a plugging problem. However, any deposits which form can be easily removed by water washing. Since almost all preheater designs incorporate equipment for water washing, no special modifications are required to remove deposits. In most cases, the preheater is only washed during boiler outages, but operating data from Japan indicate that, in some SCR and SNR installations, deposit build-up is so severe that boiler outages are required just to wash the preheater.³

To minimize or eliminate the potential for forced boiler outages due to $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition, the boiler-air preheater design should incorporate provisions for in-service water washing. The preheater can be washed in-service by one of two methods: 1) isolated washing and, 2) on-stream washing.

Isolated washing involves washing one air preheater (in a multiple air preheater installation) while the boiler is at reduced load. The air preheater to be washed is isolated by closing dampers and shutting down fans. This washing procedure works well in keeping the preheater clean and usually requires only 4 to 16 hours to complete. For many units, isolated washing can be conducted during normal load reduction in "off-peak" hours.⁶

On-stream washing is carried out while both flue gas and air are flowing through the preheater. However, it is only applicable in installations where the duct work and drains are designed to minimize the amount of moisture which is entrained in the combustion air and flue gas. On-stream washing must be initiated before deposit build-up reaches the point where plugging of gas passages occurs. For Ljungstrom type preheaters, the manufacturer recommends that on-stream washing be initiated once the gas-side pressure drop in the preheater increases by .12 kPa (0.5 in H₂O).⁶

Use of either isolated or on-stream washing should prove effective in eliminating (NH₄)₂SO₄/NH₄HSO₄ deposits from air preheaters. In addition, employing these washing techniques will prevent a forced boiler outage due to deposit formation. From a design and operation standpoint, isolated washing appears to be the best suited technique. No special design modifications are required and the required cleaning frequency should be lower. Also, less wastewater will be generated and so treatment costs (if any) will be minimized.

The required water washing frequency to control deposit build-up will depend on the concentrations of NH₃ and SO₃ in the flue gas. Based on reports of Japanese experience, the frequency will range from 3 to 6 months. Use of in-service washing at three-month intervals should not present any major problems while minimizing deposit build-up.

Use of Corrosion Resistant Material in the Intermediate and Low Temperature Zones of the Preheater

Available information indicates that intensive soot blowing and water washing will minimize deposit build-up and prevent forced boiler outages. However, data from laboratory and pilot plant tests and the results of air preheater deposit analyses indicate that corrosion of the preheater can present a significant problem. Also, the results of Radian's thermodynamic analysis, supported by experimental evidence, indicate that both deposit formation and corrosion begin in the intermediate temperature zone of the preheater. This presents a problem with a conventional air preheater design.

Most regenerative air preheaters are designed so corrosion can occur only in the extreme cold-end of the preheater. Typically, the impact of this is minimized by use of heavy-gauge (~ 1.25 mm) heat transfer elements which are more resistant to corrosion. In addition provisions exist for easy removal and replacement of the extreme cold-end elements.

Corrosion in the intermediate temperature zone presents several problems. First, these elements are typically thin steel (~ 0.56 mm) and therefore particularly vulnerable to corrosive attack. Second, replacement of elements in the intermediate temperature zone may represent a difficult maintenance problem. The obvious solution to this problem is to use corrosion resistant material in the intermediate zone of the preheater. There are two options which can be employed. Heavy-gauge, mild steel similar to that used in the cold-end can be used or corrosion resistant steel (e.g. 304 SS or enamel coated steel) can be installed.

The choice of material is an economic one and will depend on several factors. Use of heavy-gauge steel will minimize but not eliminate corrosion and it may be necessary to periodically replace the intermediate temperature elements. The information available on the difficulty of replacing these

elements indicates that it should not be difficult. Based on the test results reported by EPDC, it appears that intermediate temperature zone elements would have to be replaced every 5 to 10 years.⁸ The cost of this replacement (materials, maintenance effort, and outage time) would have to be balanced against the initial costs of using corrosion resistant material to determine the most economical solution.

For this evaluation, 304 SS is assumed to be the material used in the combined intermediate/low temperature zone of the preheater. Since the use of mild steel entails several variables which cannot be readily quantified and enamel coated steel is relatively inexpensive, the use of SS represents a conservative approach. But, according to corrosion data, 304 SS should provide acceptable service in the preheater.

Estimated Energy Consumption for Air Preheater Design Options

Use of available air preheater design options to minimize the impacts of deposit formation will result in an increase in the energy required to operate the air preheater. This increase in energy consumption (as compared to the base case) is presented in Table 6-2 for each of the changes in air preheater design/operation. No energy consumption is presented for water washing since this represents a very small fraction of the soot blowing energy requirements. No energy penalty is incurred due to the use of combined heat transfer elements.

As shown in Table 6-2, the largest increase in energy consumption results from the additional number of soot blowers and the second largest increase results from the increased soot blowing frequency. Increasing soot blowing pressure only has a small impact on the energy consumption. Overall, the air preheater modifications result in a twelve-fold increase in energy consumption and about a 0.2 percent decrease in the efficiency of the boiler.

TABLE 6-2. ENERGY CONSUMPTION FOR DESIGN OPTIONS

Option	Relative Energy Consumption		Energy Consumption (MW _t)	
	Base Case	Option	Base Case	Option
Steam Pressure	1.0	1.01	0.278	0.282
Number of Soot Blowers	1.0	6.0	0.278	1.67
Soot Blowing Frequency	1.0	2.0	0.278	0.556
TOTAL	1.0	12.12	0.278	3.37

Estimated Capital and Annualized Costs for Air Preheater Design Options

Table 6-3 presents estimated annualized costs for each of the design options which incur an incremental cost. In addition, incremental capital costs are shown. The most significant fraction of these costs results from the increased steam consumption due to the additional soot blowers and the increased soot blowing frequency. A second cost on the same order is the annualized cost associated with use of 304 stainless steel for the intermediate temperature zone elements in the preheater. Based on available data, it does not appear that the use of the modified heat transfer element design will significantly increase the capital or operating costs of the preheater. Consequently, Table 6-3 does not include increased costs for this modification.

The costs presented in Table 6-3 are rough estimates and are included to provide a basis for comparing the use of air preheater design options with other solutions to the deposition problem. These costs are based on a new rather than a retrofit installation. To determine actual costs, several issues must be resolved by conducting tests to determine the requirements/effectiveness of each air preheater design option. In addition, more detailed vendor quotes for equipment are required. It should be noted that the costs for the preheater design options presented here are about 1.6 times

the cost of the base case. This compares to an estimate of 1.5 times base costs estimated by Gadelius in Japan.

TABLE 6-3. ESTIMATED CAPITAL AND FIRST YEAR ANNUALIZED COSTS FOR AIR PREHEATER DESIGN OPTIONS¹

Option	Incremental Capital Costs (\$1000)	Incremental Annualized Costs (\$1000)
Soot Blowing Modifications	158	233
In-Service Washing	0	18
Corrosion Resistant Material	1376	201
TOTAL	1534	452

¹Cost Basis: 1979 capital costs/1980 annualized costs - other details are presented in Appendix C.

6.1.2 Heat Cleaning of Deposits

The fact that $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposits can decompose at elevated temperatures provides the basis for a second solution to the deposition problem. This solution, termed "heat cleaning", requires that the cold-end metal temperature in the preheater be elevated to the point where $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 will rapidly decompose (350 to 450°C).¹⁸ Periodic cleaning using this technique should help prevent deposit build-up.

The frequency and duration of the cleaning cycle will depend on the rate at which deposits accumulate and the effectiveness of the heat cleaning procedure. For this evaluation, the preheater will be heat-cleaned once per day during "off-peak" hours. The duration of the cleaning cycle will be 30 minutes per preheater which should permit complete decomposition of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposits. This duration was selected based on laboratory work which indicated that $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 decompose at a rate of 10 percent per minute above 350°C.

Use of the heat cleaning technique has several drawbacks. First, the elevation of preheater temperatures will result in a temporary decrease in boiler efficiency. Second, depending on the method of heat cleaning, the flue gas which exits the preheater may need to be cooled to prevent damage to downstream equipment due to the high temperature of the gas. Cooling the gas may also be required to recondense the $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ so these compounds can be collected in particulate control equipment. Finally, heat cleaning will not be effective in removing deposits of $\text{NH}_4\text{-Fe-SO}_4$ compounds and $\text{NH}_4\text{-fly ash-SO}_4$ compounds which can form in the preheater.

The use of heat cleaning requires that several modifications be made to the preheater including:

- Method/equipment for raising cold-end metal temperature in the air preheater,
- Method/equipment for cooling gas upstream of particulate collection equipment, and
- Use of corrosion resistant material in the intermediate/low temperature zone of the preheater

It should be noted that no data are available which indicate if heat cleaning will work or how effective it will be. This evaluation is strictly based on engineering judgement and requires experimental work to substantiate the results. In ranking the technical feasibility of this solution, it should be considered as possible but not proven.

The following discussion examines each of the modifications required to permit heat cleaning of an air preheater. In addition, the increased energy consumption is estimated and capital and annualized costs for heat cleaning are presented.

Modifications Required to Permit Heat Cleaning

Use of heat cleaning to minimize air preheater deposits requires that several modifications be incorporated in the air preheater design. In particular, these modifications must include provisions for increasing the cold-end metal temperature. Examination of air preheater design characteristics indicates three possible methods of increasing the cold-end metal temperature are: 1) to decrease the heat transfer efficiency of the air preheater, 2) to increase the temperature of the air entering the preheater, or 3) eliminate the flow of air to the preheater while reducing the flue gas flow rate.

The heat transfer efficiency of the preheater is a complex function of gas and air flowrates and air preheater design characteristics including rotation speed of the heat transfer elements.⁷ By decreasing the rate of the preheater's rotation, the heat transfer efficiency will decline and the average cold-end metal temperature can be increased. This is a relatively easy change since provisions usually exist to permit adjustment of the preheater rotation speed. However, there are several problems with this procedure.

First, a large decrease in rotation speed is required to produce a significant change in the thermal efficiency of the preheater. This can result in thermal gradients in the flue gas exiting the preheater which can adversely impact the operation of downstream ESP equipment. Second, a decrease in an air preheater's rotation speed will increase the cold-end metal temperature but it will also decrease the combustion air temperature. This could present problems in a coal-fired boiler where preheated air is routed to the pulverizers to dry the coal. If the coal is not adequately dried or if the combustion air is too cold, problems could result. Finally, a decrease in rotation speed may also have an adverse impact on the air preheater equipment. By decreasing the rotation speed, the temperature fluctuations experienced in the preheater will increase. This results

in differential expansion of the preheater wheel and could cause thermal stress on the rotor and excessive wear of the seals which prevent leakage of air into the gas.

A second method of increasing the cold-end metal temperature is to increase the air temperature entering the preheater. Most air preheater designs do have provisions for raising the air temperature using a steam coil heat exchanger. This helps minimize fluctuations in the cold-end metal temperature due to changes in ambient temperature. A similar technique can be used for heat cleaning. A larger steam coil could be installed at the cold-end of the air preheater and the entering air temperature increased during the cleaning period. This technique would minimize the temperature difference between the gas and air sides of the preheater and thus prevent unusual seal wear.

The third technique for raising the air preheater operating temperature appears to be the most promising. By stopping the flow of air to the preheater and reducing the flue gas flow, the preheater temperature can be raised to the flue gas temperature with a minimum of problems. Since no air flows through the preheater during this period, the effects of differential expansion of the preheater wheel would be minimized. Also, operation at a reduced flue gas flow will minimize the decline in boiler efficiency and it may not be necessary to cool the flue gas exiting the preheater with dilution air. The principal problem with this technique appears to be the requirement for isolation of the preheater which may necessitate a reduction in boiler load. For the case examined in this study, it should be possible to isolate and clean one preheater with about a one-third reduction in boiler load.

Because isolation of a preheater appears to be the best technique for heat cleaning, the following discussion will be limited to examining this option.

Modifications Required to Cool Flue Gas During Heat Cleaning Cycle

During heat cleaning, the flue gas temperature at the exit of the air preheater being cleaned will be 350 to 400°C. This could present problems with downstream equipment including ESP's and baghouses if the flue gas is not cooled. The elevated temperature can reduce ESP efficiency by increasing the resistivity of fly ash. It can also distort the electrodes in the precipitator due to thermal expansion and possibly cause permanent damage. In the case of fabric filters, most filter media are not capable of withstanding temperatures of 350°C and would fail during heat cleaning. A potential environmental problem could also result from heat cleaning. Any NH_3 and $\text{SO}_3/\text{H}_2\text{SO}_4$ vapor which is produced during the heat cleaning cycle could be emitted from the stack, recondense, and produce a visible plume.

In order to prevent equipment problems and to minimize NH_3 and $\text{SO}_3/\text{H}_2\text{SO}_4$ emissions, the flue gas from the preheater may need to be cooled during the heat cleaning cycle. The simplest way to cool the gas is to employ ambient air for dilution as shown in Figure 6-2. This would prevent excessive temperatures in downstream equipment. In addition, it would recondense $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$. Available data indicate that the ammonium sulfates will be collected by a downstream precipitator, although there are no data on the effect of ammonium sulfates on baghouse performance.²³

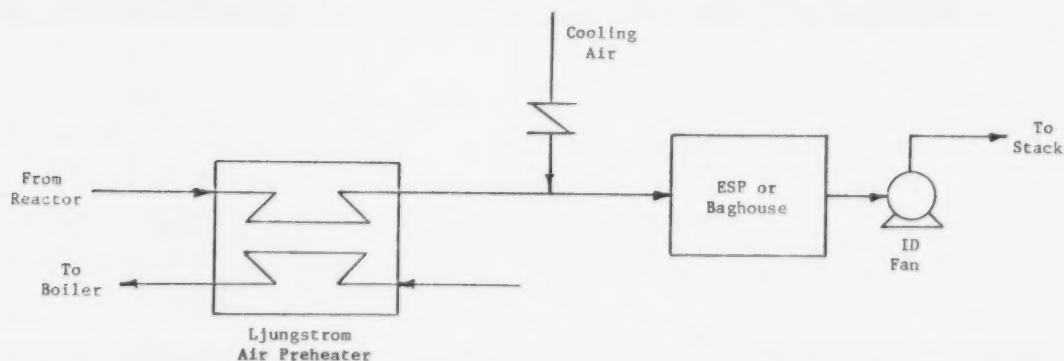


Figure 6-2. Schematic of air dilution for heat cleaning cycle.

If a preheater can be isolated and cleaned at a flue gas flow rate of approximately 10 percent of design while the other preheater operates at 150 percent of design flow, it should be possible to heat clean the preheater without cooling the flue gas downstream. However, if heat cleaning requires a flue gas flow rate of 20 percent or more of design, it may be necessary to use dilution air to cool the flue gas. For purposes of evaluating the costs of heat cleaning, it will be assumed that no dilution air is required during the cleaning cycle. Unfortunately, the only way this assumption can be verified is to conduct tests in which heat cleaning is examined on a pilot or full scale regenerative preheater.

Modifications Required to Permit Isolation of the Preheater for Cleaning

Use of heat cleaning to remove deposits of ammonium sulfates will require that the preheater be completely isolated on the air side while flue gas is admitted at a reduced rate. This will require the addition of isolation/flow control dampers and a flow control system for the flue gas. Estimates for the incremental capital costs of the dampers and the control system are presented in Appendix C.

Use of Corrosion Resistant Material in the Intermediate and Low Temperature Zones of the Preheater

Heat cleaning of the air preheater will remove any deposits of $(\text{NH}_4)_2\text{SO}_4$ / NH_4HSO_4 which may be present. However, formation of $\text{NH}_4\text{-Fe-SO}_4$ corrosion products will produce deposits which cannot be removed by heat cleaning. In addition, corrosion of the intermediate temperature zone heat transfer elements will not be prevented by heat cleaning. For these reasons, corrosion resistant material should be used in the intermediate and low temperature zones of the preheater. This should prevent or minimize formation of corrosion products which cannot be removed by heat cleaning. In addition, it should eliminate any requirement for replacement of the heat transfer elements.

Use of corrosion resistant material will result in an incremental cost of the preheater. For reasons discussed in Section 6.1.1, 304 stainless steel was selected for this evaluation and the estimated costs are presented in Appendix C.

Estimated Energy Consumption for Air Preheater Heat Cleaning

Use of heat cleaning will result in a slight decrease in boiler efficiency due to the increase in flue gas temperature exiting the air preheater during the cleaning cycle. The energy penalties associated with heat cleaning have been estimated to be $.27 \text{ MW}_t$. This represents an instantaneous decrease in boiler efficiency of about 1 percent during the cleaning cycle and an average decrease of .02 percent. Details of the calculations which estimate this energy penalty are contained in Appendix C.

Estimated Capital and Annualized Costs for Heat Cleaning

Use of heat cleaning will result in increased capital and annualized costs for the boiler-air preheater SCR system. The capital costs result primarily from use of corrosion resistant material in the intermediate temperature zone of the preheater. Capital costs are also expected due to design modifications required to isolate and permit heat cleaning of the preheater. Operating costs will be associated with the energy consumption during the heat cleaning cycle.

Table 6-4 presents estimated incremental capital and annualized costs for heat cleaning. As shown, the capital and annualized costs associated directly with the heat cleaning cycle are about one-fourth the capital and annualized costs for corrosion resistant material. It should be noted that the costs presented in Table 6-4 are rough estimates. In addition, it is uncertain whether heat cleaning can be employed without impacting air preheater design or even if heat cleaning will be effective in removing deposits. This can only be

determined by more detailed investigation. Therefore, caution should be exercised in applying the results of the economic analysis presented here.

TABLE 6-4. ESTIMATED CAPITAL AND FIRST YEAR ANNUALIZED COSTS FOR AIR PREHEATER HEAT CLEANING¹

Option	Incremental Capital Cost (\$1000s)	Incremental Annualized Cost (\$1000s)
Heat Cleaning	370	70
Corrosion Resistant Material	1376	201
TOTAL	1746	271

¹Cost Basis: 1979 capital costs/1980 annualized costs - Other details are presented in Appendix C.

6.1.3 Flue Gas Recirculation

There are several aspects of the $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ formation reactions which can be exploited to minimize or possibly eliminate the deposition problem. First, $(\text{NH}_4)_2\text{SO}_4$ forms at higher temperatures than NH_4HSO_4 and in pure form exists only as a solid. Second, at 20°C below the initial formation temperature, the $(\text{NH}_4)_2\text{SO}_4$ formation reaction can proceed to approximately 80 percent completion while no NH_4HSO_4 should form. Use of flue gas recirculation is one method of preventing deposit formation. By careful design of the air preheater system, it may be possible to selectively form $(\text{NH}_4)_2\text{SO}_4$, minimize deposit formation, and improve boiler efficiency. Flue gas recirculation employs flue gas from downstream of the air preheater to cool hot flue gas in a reaction chamber. Temperatures are controlled in the chamber so $(\text{NH}_4)_2\text{SO}_4$ is formed but no NH_4HSO_4 forms.

There are two preheater designs which can be employed with flue gas recirculation; single and split. The split design divides a single air preheater into two preheaters in series separated by a reaction chamber as

shown in Figure 6-3. The first air preheater is operated such that the cold-end metal temperature is maintained above the $(\text{NH}_4)_2\text{SO}_4$ formation temperature. Cooled flue gas is recirculated from downstream of the second preheater and injected into the reaction chamber. The recirculation rate is controlled so the flue gas in the reaction chamber is cooled below the $(\text{NH}_4)_2\text{SO}_4$ formation temperature but not below the NH_4HSO_4 formation temperature. This results in the formation of solid $(\text{NH}_4)_2\text{SO}_4$ particles which can pass through the second air preheater and be collected in downstream particulate removal equipment. As shown in Figure 6-3, flue gas is recirculated from upstream of the particulate collection equipment even though this requires the recirculation fan to operate under high particulate loadings. The reason for this is to minimize the flue gas flow rate entering the particulate collector thus minimizing particulate control costs.

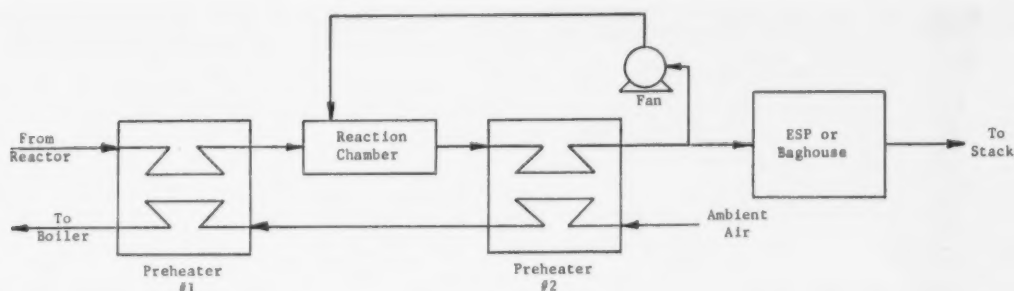


Figure 6-3. Schematic of split-air preheater design.

An alternative to the split air preheater design is a single air preheater in which flue gas is recirculated from the cold-end to a reaction chamber upstream of the hot-end. The recirculation rate is controlled to maintain the flue gas temperature entering the preheater below the $(\text{NH}_4)_2\text{SO}_4$ formation temperature but above the NH_4HSO_4 formation temperature. In principle, this technique is identical to use of a split air preheater. However, in practice, the costs would be somewhat different. Use of a single preheater would require recirculation of more flue gas and would require more heat transfer material overall.

Flue gas recirculation was identified as a possible solution to the deposition problem based strictly on the results of Radian's thermodynamic analysis of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ formation. However, there are other factors which make the feasibility of this solution uncertain. First, there are no data on the rate at which $(\text{NH}_4)_2\text{SO}_4$ forms from gas phase reactants. All experimental data, including analysis of air preheater deposits, indicate that NH_4HSO_4 is the first product to form from gaseous reactants. The results of Radian's kinetic analysis confirms that the NH_4HSO_4 formation reaction occurs very rapidly but the $(\text{NH}_4)_2\text{SO}_4$ formation rate could not be determined. Therefore, it may be impossible to selectively form $(\text{NH}_4)_2\text{SO}_4$ with a realistically sized reaction chamber residence time (i.e., 1 to 2 sec.).

A second problem associated with flue gas recirculation is one of process control. Changes in the temperature entering the preheater due to changes in boiler load should not present a problem since the recirculation rate will be adjusted to maintain a specific temperature in the reaction chamber. The difficult part of the control system will be to determine what temperature to maintain in the reaction chamber. Changes in fuel sulfur content or excess air to the boiler may change the SO_3 concentration while changes in flue gas flow rate and NO_x concentration can change the concentration of NH_3 which is emitted from the reactor. This can result in changes in both the $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 formation temperatures which will require changes in the reaction chamber operating temperature. Determination of the operating temperature as NH_3 and/or SO_3 concentrations change requires monitoring flue gas NH_3 and SO_3 concentrations and then calculation of formation temperatures.

The problems associated with use of flue gas recirculation present significant technical obstacles. No data are available to indicate whether it is possible to selectively produce $(\text{NH}_4)_2\text{SO}_4$ in an air preheater system without first producing NH_4HSO_4 . In addition, the control problems associated with changing NH_3 - SO_3 concentrations will be difficult to resolve. Also, the space required for a reaction chamber and recirculation ducts may be extremely

difficult to incorporate into the boiler design. Therefore, flue gas recirculation is not considered a technically feasible method of preventing or minimizing deposit formation. Further work is required to determine if $(\text{NH}_4)_2\text{SO}_4$ can be produced selectively under realistic flue gas duct residence times.

Material and Energy Balances for Flue Gas Recirculation

For purposes of this evaluation, material and energy balance calculations were performed for both flue gas recirculation design options. Although flue gas recirculation may not prove technically feasible, the results of the energy balance calculations indicate that significant energy savings can be realized and the use of these techniques bears further investigation. In fact, it may be possible to realize an overall cost savings using flue gas recirculation.

Table 6-5 presents the results of material and energy balance calculations for both flue gas recirculation options. As shown, use of a split air preheater design results in a net energy savings of 18.5 MWt or a 1.4 percent improvement in boiler efficiency. Use of a single air preheater results in an energy savings of 9.1 MWt or a 0.7 percent improvement in boiler efficiency. The difference between the two options result from the requirement for recirculation of over twice as much flue gas in the single air preheater design.

The results presented in Table 6-5 were based on several assumptions which are defined with other calculational procedures in Appendix C. The principal difference is the flue gas temperature at the preheater exit. For the base case, this temperature is 150°C which corresponds to a cold-end metal temperature of 100°C. For the flue gas recirculation cases, the gas temperature at the preheater exit is assumed to be 115°C which corresponds to a cold-end metal temperature of 65°C. This low (relative to the base case) cold-end metal temperature was selected because no H_2SO_4 condensation is expected in the air preheater or downstream equipment due to the formation of $(\text{NH}_4)_2\text{SO}_4$ upstream of the preheater.

TABLE 6-5. ESTIMATED FLOW RATES AND ENERGY SAVINGS
FOR FLUE GAS RECIRCULATION

Stream	Flowrate (g/sec)	Energy Savings (loss) (MWt)
<u>Base Case</u>		
Flue Gas From Preheater	$6.2 \cdot 10^5$	0
Recirculated Flue Gas	0	0
<u>Single Preheater</u>		
Flue Gas From Preheater	$6.2 \cdot 10^5$	22.7
Recirculated Flue Gas	$1.3 \cdot 10^6$	(13.6)
<u>Split Preheater</u>		
Flue Gas From Preheater	$6.2 \cdot 10^5$	22.7
Recirculated Flue Gas	$5.8 \cdot 10^5$	(4.2)

Estimated Capital and Annualized Costs for Flue Gas Recirculation

Use of flue gas recirculation is a potential solution to the $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition problem which may not prove technically feasible. This technique relies on selective production of $(\text{NH}_4)_2\text{SO}_4$ and requires extensive modification of air preheater design. These modifications result in incremental capital costs for air preheaters, fans, and ductwork. But, flue gas recirculation can also reduce operating costs by improving boiler efficiency.

Table 6-6 presents estimated incremental capital and annualized costs for two flue gas recirculation options. These costs are based on the estimates of energy savings and on estimated capital costs described in Appendix C. As shown, the use of the split preheater design has lower capital and annualized costs than a single preheater. In fact, the cost estimates indicate that the use of a split preheater will result in a net reduction in annualized costs due to the energy savings associated with this option. The reader is cautioned that these costs are rough estimates. The actual cost for a split air preheater must be determined through detailed analysis.

In addition, there are no data which indicate that $(\text{NH}_4)_2\text{SO}_4$ can be selectively formed at a rate compatible with residence times in a realistically sized reaction chamber. Experimental investigation of $\text{NH}_3\text{-SO}_3$ reactions is required to determine the feasibility of using flue gas recirculation.

TABLE 6-6. ESTIMATED CAPITAL AND FIRST YEAR ANNUALIZED COSTS FOR FLUE GAS RECIRCULATION¹

Method	Incremental Capital Costs (\$1000's)	Incremental Annualized Costs (\$1000's)
Single Preheater	9690	857
Split Preheater	6223	(198)

¹Cost Basis: 1979 capital costs/1980 annualized costs - Other details presented in Appendix C.

6.1.4 Increased Cold-End Metal Temperature in the Air Preheater

Condensation of H_2SO_4 in an air preheater can result in deposit formation, plugging, and corrosion of an air preheater. The problem can be eliminated by increasing the cold-end metal temperature above the H_2SO_4 dew-point. This method can also be used to eliminate deposits due to $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ formation. By increasing the cold-end metal temperature in the preheater above the NH_4HSO_4 formation temperature, the deposition of liquid NH_4HSO_4 can be prevented. This will minimize plugging and corrosion since any $(\text{NH}_4)_2\text{SO}_4$ which deposits should exist as a solid. These deposits will not corrode the preheater or tend to collect fly ash.

Available operating experience indicates that raising the air preheater outlet temperature can eliminate formation of deposits. However, no data are available for cases where the cold-end metal temperature is below the $(\text{NH}_4)_2\text{SO}_4$ formation temperature but above the NH_4HSO_4 formation temperature. Therefore, it is uncertain if deposition of $(\text{NH}_4)_2\text{SO}_4$ will present a serious problem. Additional investigation of the $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ formation reactions is needed to determine if deposition of $(\text{NH}_4)_2\text{SO}_4$ can be tolerated.

For purposes of this evaluation, it is assumed that maintaining the cold-end metal temperature in the preheater above the NH_4HSO_4 formation temperature will eliminate the problem of plugging and corrosion which have been experienced downstream of SCR and SNR installations. Modification of the air preheater design to permit operation with a higher cold-end metal temperature should be relatively simple. The principal change required is a reduction in thermal efficiency of the preheater. Efficiency can be reduced by reducing the size of the preheater so the cold-end temperature is above the NH_4HSO_4 formation temperature.

In addition to reducing the overall size of the preheater, some modification of the basic design may be required. In the case of pulverized coal firing, it will be necessary to maintain the primary air temperature at the base case design level. This will require increasing the size of the primary air passages through the preheater relative to the secondary air passages. To determine the exact changes which will be required, it will be necessary to consult a manufacturer and complete a detailed air preheater design. However, the required changes are not expected to increase the capital cost of the air preheater and in fact, they may slightly decrease costs.

The principal impact of increasing the cold-end metal temperature will be to decrease boiler efficiency as discussed in Section 3.0. In addition, there may be some impacts on downstream equipment and possibly an environmental impact due to gas phase NH_3 and SO_3 emissions (Section 6.1.2). For these reasons, a damper should be installed to permit cooling of the flue gas to 190°C with ambient air. This will minimize impacts on downstream equipment. It will also result in production of solid $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ which can be collected in an ESP.

Energy Balance For Increasing Cold-End Metal Temperature in an Air Preheater

Increasing the cold-end metal temperature of the air preheater above the formation temperature of NH_4HSO_4 will result in a significant energy

loss in the flue gas exiting the stack. This corresponds to an equivalent decline in boiler thermal efficiency and an increase in annual fuel costs.

Table 6-7 presents estimates of the energy loss which results when the cold-end metal temperature is increased to prevent NH_4HSO_4 formation for 30 ppm NH_3 and 10 ppm SO_3 in the flue gas. For comparison, the energy loss which results when $(\text{NH}_4)_2\text{SO}_4$ formation is prevented is also presented. As shown, prevention of NH_4HSO_4 formation results in an energy loss of 51.9 MWt or a 3.9 percent reduction in boiler efficiency while prevention of $(\text{NH}_4)_2\text{SO}_4$ formation results in a loss of 71.4 MWt or a 5.4 percent reduction in boiler efficiency.

TABLE 6-7. ESTIMATED ENERGY CONSUMPTION WHICH RESULTS FROM INCREASING AIR PREHEATER EXIT TEMPERATURE

Option	Outlet Gas Temperature ($^{\circ}\text{C}$)	Energy Loss (MWt)
Base Case	150	0
Prevent NH_4HSO_4 Formation	230	51.9
Prevent $(\text{NH}_4)_2\text{SO}_4$ Formation	260	71.4

The magnitude of the energy penalty associated with increasing the cold-end metal temperature will change as NH_3 and SO_3 concentrations in the flue gas change. Figure 6-4 illustrates energy penalty required to prevent NH_4HSO_4 formation as a function of NH_3 concentration for constant SO_3 concentration. As shown, the slope of this curve is very small and even at 1 ppm NH_3 , the estimated energy penalty is 36.7 MWt. Obviously, this does not agree with experimental evidence which indicates that at NH_3 concentrations below 10 ppm, only minor deposition problems are encountered.

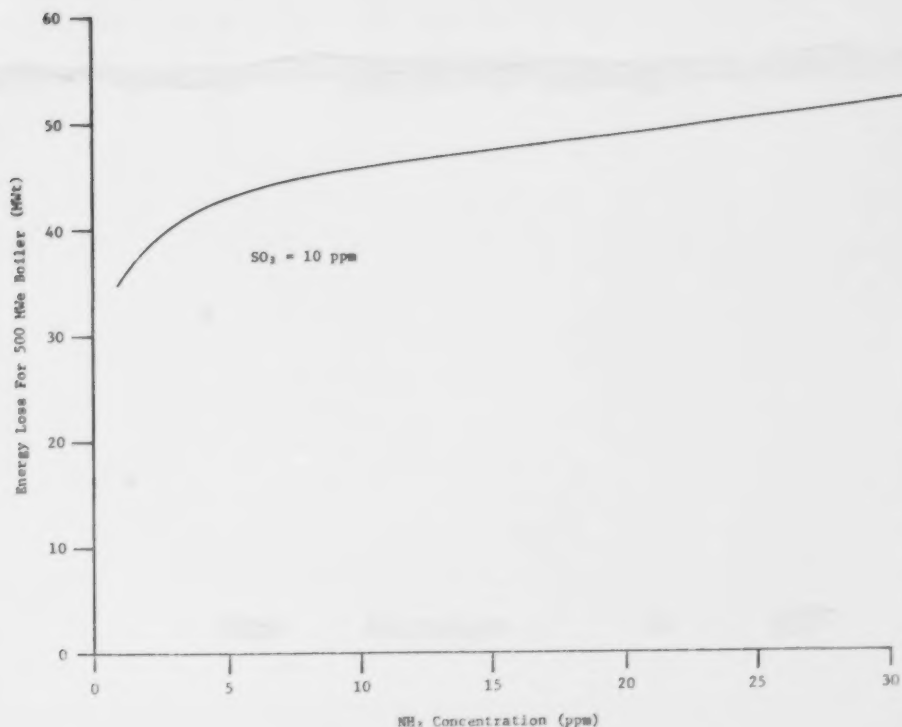


Figure 6-4. Estimated energy loss required to prevent NH_4HSO_4 condensation as a function of flue gas NH_3 concentration.

There are several possible explanations for the discrepancy between practice and the predicted problems. It may be that actual formation temperatures are below those predicted by the thermodynamic analysis. This could be due to an energy barrier which must be overcome for formation to occur or it is possible that the thermodynamic data used in the analysis are somewhat in error. It is also possible that low concentrations of NH_3 form deposits which can be scoured by particulates in the flue gas or the deposits may be more readily removed by soot blowing since they will form closer to the cold-end of the preheater where the soot blowers are located.

The reason why low NH_3 concentrations do not result in deposition problems is unclear. However the fact that low NH_3 emissions do not present serious problems is documented by Japanese experience. This phenomenon will

influence the energy penalties experienced when raising the cold-end metal temperature to prevent deposition and should be quantified. This requires that further experimental work be conducted to investigate what combinations of NH_3 and SO_3 concentrations and outlet air preheater temperatures will or will not result in deposition problems.

Estimated Capital and Annualized Costs for Increasing Air Preheater Cold-End Temperatures

Increasing the air preheater outlet temperature will result in increased operating costs for the boiler due to the change in thermal efficiency. However, no increase in capital costs is expected. In fact, capital costs may be reduced since a smaller air preheater will be used to increase the outlet temperature.

The annualized costs for increasing the air preheater exit temperature are presented in Table 6-8. Costs are presented for preventing both NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$ formation. As shown, the cost for preventing NH_4HSO_4 formation is approximately 70 percent of the cost which results from preventing $(\text{NH}_4)_2\text{SO}_4$ formation. This represents a difference of over \$1,000,000 per year in fuel costs. Details of how these costs were determined are presented in Appendix C.

TABLE 6-8. ESTIMATED ANNUALIZED COSTS FOR INCREASING AIR PREHEATER EXIT TEMPERATURE¹

Option	Incremental Annualized Costs (\$1000s)
Base Case	0
Prevent NH_4HSO_4 Formation	3,098
Prevent $(\text{NH}_4)_2\text{SO}_4$ Formation	4,270

¹Cost Basis: 1980 annualized costs - Other details presented in Appendix C.

6.2 MODIFICATION OF SCR SYSTEM DESIGN/OPERATION

Modification of air preheater design and operation represents one general approach to solving the $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition problem. A second approach to solving this problem is to modify the SCR system design and/or operation. The intent of modifying the SCR system is to reduce the NH_3 emissions from the reactor, thereby reducing the formation of ammonium sulfates in the preheater. In various SCR operations, NH_3 concentrations below 10 ppm have been shown to minimize deposit formation.

There is basically one way to modify the SCR system so that the NH_3 emissions are reduced. Additional catalyst can be added to the reactor and NH_3 injection rate can be lowered while maintaining the desired NO_x removal level, thus reducing the NH_3 emissions. Another alternative which has been examined by Japanese SCR system vendors is the addition of an ammonia decomposition catalyst downstream of the reactor. However, this idea has apparently been abandoned in favor of the first alternative. The following discussion examines the effects of increasing the catalyst charge and decreasing the NH_3 injection rate but does not consider an NH_3 decomposition catalyst.

Increasing Quantity of Catalyst While Maintaining Constant NO_x Removal Efficiency

The design of an SCR system is influenced by a trade-off between the quantity of catalyst in the reactor, the NH_3 injection rate, and the NO_x removal efficiency of the system. The value of each design parameter will be determined by its impact on the annual costs of operating the system, regulatory requirements on NO_x emissions, and the requirement for preventing excessive NH_3 emissions. Without regard for system costs, these parameters can be adjusted to maintain a constant NO_x removal efficiency while minimizing NH_3 emissions.

By increasing the quantity of catalyst while simultaneously reducing the NH_3 injection rate, the NH_3 emissions can be reduced. This relationship is quantified in Table 6-9.

TABLE 6-9. EFFECT OF INCREASED CATALYST ON NH_3 EMISSIONS

Case	Base	1	2	3
Relative Catalyst Amount	1.0	1.10	1.31	1.71
NH_3/NO_x for 90% Removal	1.0	0.98	0.95	0.92
Estimated NH_3 Emissions (ppm)	30	20	10	0

As shown, NH_3 emissions for the base case are 30 ppm. Approximately 40 percent additional catalyst is required to reduce NH_3 emissions below 10 ppm while 70 percent more catalyst should eliminate NH_3 emissions entirely. The estimated minimum NH_3/NO_x mole ratio is 0.92. Details of how the relative amount of catalyst and NH_3/NO_x ratios were determined are presented in Appendix C.

The most significant impact of increasing the amount of catalyst in the reactor will be to increase the costs of operating the SCR system. This results from the requirement for replacing the catalyst at regular intervals. Increasing the amount of catalyst will also result in a slight reduction in the NH_3 consumption for the system. No significant energy penalties will result from increasing the catalyst quantity.

Estimated Capital and Annualized Costs For Increasing the Quantity of Catalyst

There are several capital costs associated with increasing the quantity of catalyst in the reactor. First there is an initial capital charge for the additional catalyst which is incurred prior to start-up of the SCR system. Second, there is the capital cost for a larger reactor to hold the additional catalyst. The annualized costs which result from use of additional catalyst include the costs for replacement of the catalyst and a reduced cost for NH_3

which results from a reduction in the NH_3/NO_x ratio required for 90 percent removal.

The costs for a 500 MW SCR system have been estimated by TVA. Using this estimate as a basis, capital and annualized costs were estimated for the three cases presented in Table 6-9. For comparison purposes, a catalyst life of 1 and 2 years was assumed, although TVA's analysis assumed a 1-year life. The resultant annualized costs are presented in Table 6-10.

TABLE 6-10. INCREMENTAL FIRST YEAR ANNUALIZED COSTS FOR INCREASING THE CATALYST CHARGE.¹

	Base case		Case 1		Case 2		Case 3	
Catalyst life (yrs)	1	2	1	2	1	2	1	2
Capital charges (\$1000/yr)	0	0	285	285	884	884	2025	2025
Catalyst replacement (\$1000/yr)	0	0	898	449	2784	1392	6377	3189
NH_3 consumption	0	0	(12)	(12)	(28)	(28)	(44)	(44)
Total (\$1000/yr)	0	0	1171	722	3640	2248	8358	5170

¹Cost Basis: 1979 Capital costs/1980 annualized costs - Other details presented in Appendix C.

As shown, these costs indicate that increasing the quantity of catalyst becomes progressively more expensive. However, in two of the three cases, NH_3 emissions have not been eliminated and deposition can still present a problem. In order to assess the cost of these NH_3 emissions, a second set of estimates was prepared and is presented in Table 6-11. In cases where NH_3 emissions are present, an annualized cost was assessed which is based on the estimated cost incurred to raise the cold-end metal temperature above the NH_4HSO_4 formation temperature.

Table 6-11 shows that for all cases the cost for increasing the quantity of catalyst and raising the cold-end metal temperature is greater than the cost

of raising the cold-end metal temperature above the formation temperature for the base-case. However, if NH_3 emissions of 10 ppm can be demonstrated to minimize deposit formation, and the cold-end temperature does not have to be raised, case 2 would have a lower annualized cost for a catalyst life of 2 years.

TABLE 6-11. INCREMENTAL ANNUALIZED COSTS FOR CATALYST, NH_3 , AND INCREASING AIR PREHEATER COLD-END METAL TEMPERATURE.¹

	Base case		Case 1		Case 2		Case 3	
Catalyst life (yrs)	1	2	1	2	1	2	1	2
Annual costs ² (\$1000/yr)	0	0	1711	722	3640	2248	8358	5170
Additional fuel cost (\$1000/yr)	3098	3098	2970	2970	2790	2790	0	0
Total (\$1000/yr)	3098	3098	4681	3692	6430	5038	8358	5170

¹Cost Basis: 1979 Capital costs, 1980 annualized costs - Other details presented in Appendix C.

²Includes capital charges, catalyst replacement and reduced NH_3 consumption. Breakdown of costs presented in Table 6-10.

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APPENDICES

APPENDIX A

THERMODYNAMIC ANALYSIS OF NH_3 REACTIONS AT AIR PREHEATER TEMPERATURES

INTRODUCTION

Radian conducted a thermodynamic analysis of NH_3 reactions which can occur at air preheater temperatures. In this analysis, formation temperatures were estimated for NH_3 reactions with other flue gas constituents. In addition, equilibrium concentrations of NH_3 and SO_3 in the flue gas were estimated as a function of temperature. This appendix presents Radian's analysis of NH_3 reactions, the results of this analysis, and a discussion of the results.

OBJECTIVES AND APPROACH

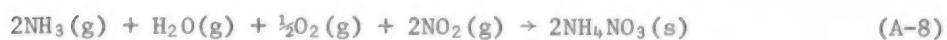
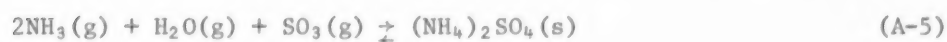
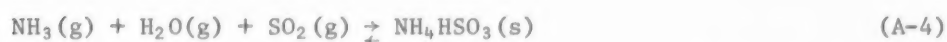
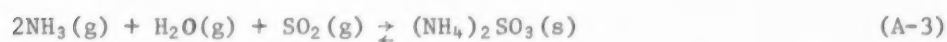
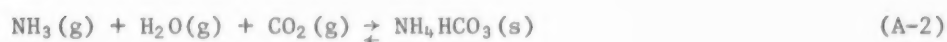
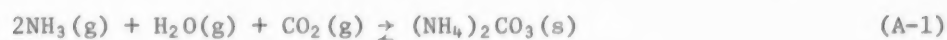
The objectives of the thermodynamic analysis of NH_3 reactions were:

- Identify what reactions can occur in the air heater.
- Determine what conditions will result in formation of ammonium sulfates and, for given inlet NH_3 and SO_3 concentrations, at what temperature does formation begin.
- Identify the type and amount of deposits formed (at and below the initial formation temperature).

This analysis employed thermodynamic principles to determine which chemical reactions can occur in an air preheater and to estimate the equilibrium concentrations of both reactants and products. The results of the analysis do not imply that the reactions which can occur will proceed at a

rapid or even measurable rate. They do, however, identify reactions which will not proceed under certain circumstances.

When ammonia is present in a flue gas, it may react with various flue gas components according to the following equations.



Consider a hypothetical flue gas with the following analysis:

O_2 = 3%
 CO_2 = 15%
 H_2O = 10%
 SO_2 = 1000 ppm
 NO = 200 ppm
 SO_3 = 20 ppm
 NO_2 = 10 ppm
 NH_3 = 20 ppm
 HCl = 50 ppm

The product formation temperatures predicted from equilibrium equations for reactions A-1 through A-9 are shown in Table A-1.

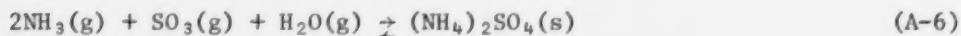
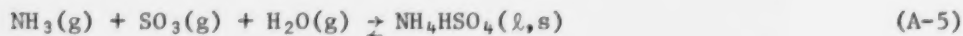
TABLE A-1. FORMATION TEMPERATURES FOR AMMONIUM COMPOUNDS
IN HYPOTHETICAL FLUE GAS

Reaction Number	Flue Gas Component	Product	Formation Temperature
A-1	CO ₂	Ammonium carbonate	< - 6°C
A-2	CO ₂	Ammonium bicarbonate	< - 21°C
A-3	SO ₂	Ammonium sulfite	< 29°C
A-4	SO ₂	Ammonium bisulfite	< 29°C
A-5	SO ₃	Ammonium sulfate	< 210°C
A-6	SO ₃	Ammonium bisulfate	< 185°C
A-7	NO	Ammonium nitrite	< -160°C
A-8	NO ₂	Ammonium nitrate	< 98°C
A-9	HCl	Ammonium Chloride	< 150°C

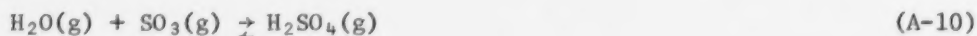
Typical air heaters have gas inlet temperatures of 300-400°C and gas outlet temperatures of 150-200°C.² As shown in Table A-1, the reactions of ammonia with flue gas constituents that occur in this temperature range are those involving SO₃ and HCl. The reaction with HCl was not considered in this analysis because it occurs in the low end of the temperature range. Additionally, if NH₃ reacts with SO₃ first (as available data suggest), the NH₄Cl formation temperature will be below air preheater operating temperatures.

The only laboratory data available on the formation of ammonia sulfates from gaseous NH₃ and SO₃ were graciously supplied to Radian by Dr. Jumpei Ando of Japan. His tests showed that the reaction product mixture was primarily ammonium bisulfate with some ammonium sulfate present.³ Another investigator reported the presence of the by-products (NH₃SO₃)₂NH and NH₃SO₃NH₂ in his ammonium sulfate production experiments.⁴ However, these compounds formed only with a reaction-limiting amount of water vapor present. A saturated flue gas (~10 percent H₂O) has a large excess of water vapor, therefore, these compounds would not form. In other studies, ammonium pyrosulfate [(NH₄)₂S₂O₇] and sulfamic acid (NH₂SO₃H) have been found to be decomposition products of ammonium sulfate.⁵ However, these products were only formed in dry atmospheres. Considering the available laboratory data and typical air pre-

heater operating conditions, the only chemical reactions involving NH_3 and SO_3 that are expected to occur are:



In addition, another related chemical reaction must be considered.



The reaction shown in equation A-10 is significant from two standpoints. First it will occur in the temperature ranges typical of an air preheater.⁶ Second, as the reaction proceeds, it lowers the concentration of SO_3 available for reaction with NH_3 (Equations A-5, A-6). As a result, the analysis of thermodynamic equilibrium considered the simultaneous equilibria of the NH_3 - SO_3 reactions and the SO_3 - H_2O reaction.

Additional data on the formation of ammonium sulfates is limited. The other data available describe the production of ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$, for use as fertilizer, via crystallization from aqueous solutions containing ammonia and sulfuric acid. Research has also been conducted in the atmospheric studies area, usually involving a liquid phase reaction (i.e., water droplets) at ambient temperatures instead of a gas phase reaction at elevated temperatures.

The most useful information available in the literature was from studies of the thermal decomposition of ammonium sulfates. These studies contained the data on heats of formation, standard entropies, and heat capacities needed to develop the thermodynamic expressions for the formation of ammonium sulfates. Figure A-1 shows the equilibrium constants for ammonium bisulfate and ammonium sulfate formation as a function of the inverse of temperature. One can see that each of the thermodynamic expressions for the free energy change of formation (ΔG_f) are quite similar. The lines shown in Figure A-1 were obtained from the following equations:⁷

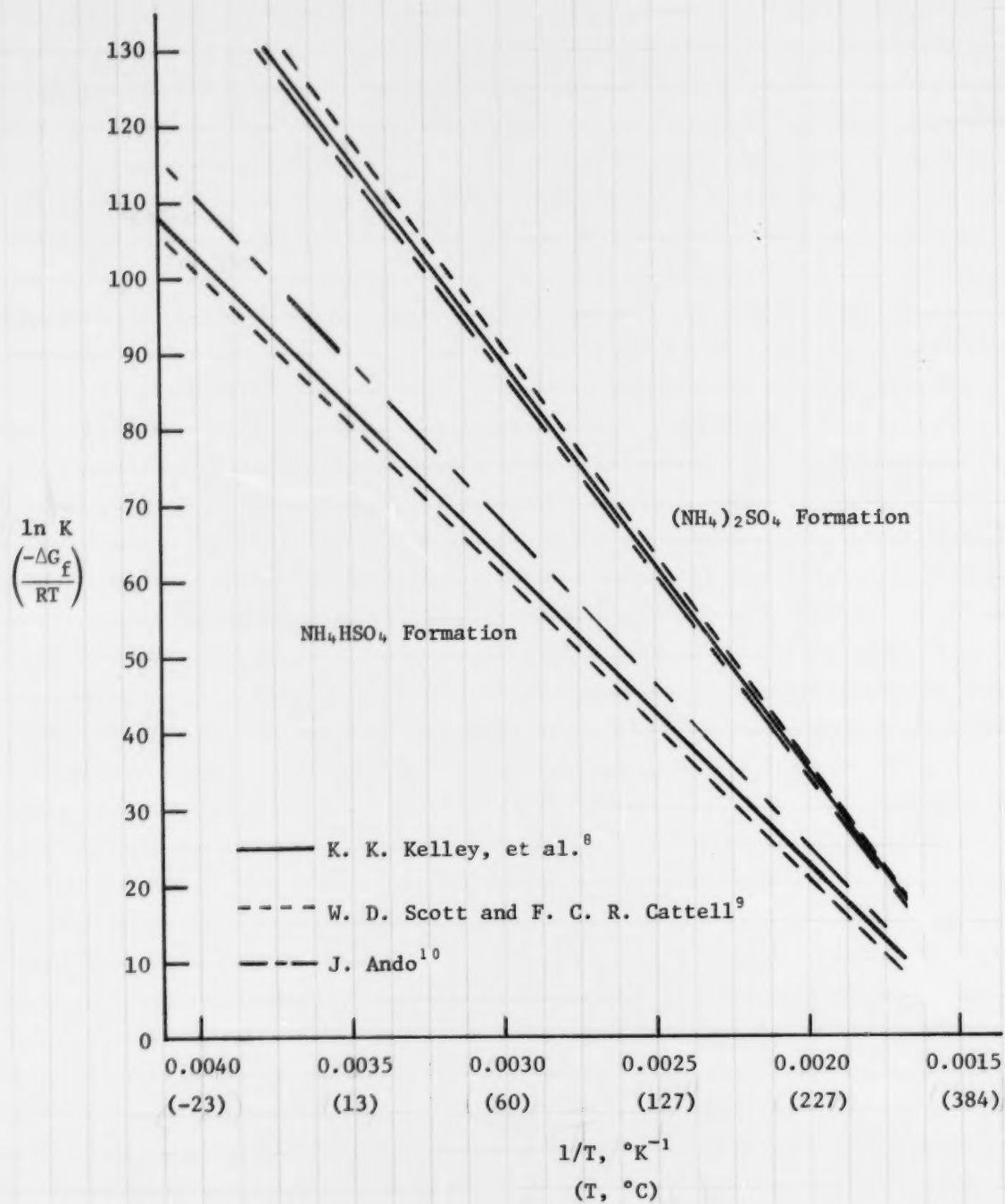


Figure A-1. Equilibrium constants for ammonium sulfate and ammonium bisulfate formation.

$$\Delta G_f = -RT \ln K \quad (\text{A-11a})$$

which can be rearranged to:

$$\ln K = \frac{\Delta G_f}{-RT} \quad (\text{A-11b})$$

Using the equation for the free energy change as a function of temperature, the equilibrium constant can be calculated at any given temperature.

Free energy is defined¹¹ by equation A-12.

$$G = H - TS \quad (\text{A-12})$$

where, G = free energy
H = enthalpy
T = temperature
S = entropy

Free energy can be thought of as the reactivity of a compound or its potential for reaction. The enthalpy term describes the thermal (heat) energy content of the compound. The entropy term describes the randomness of the compound; a highly structured, crystalline compound would have a lower entropy value while a loosely structured, gaseous compound would have a higher entropy value. All irreversible processes proceed in a direction which causes a decrease in the free energy of the system ($G_{\text{reactants}} > G_{\text{products}}$). Therefore, the free energy change for a reaction that will proceed is

$$\Delta G = G_{\text{products}} - G_{\text{reactants}} \quad (\text{A-13})$$

where

$$\Delta G < 0. \quad (\text{A-14})$$

Substituting the enthalpy and entropy terms into equation (A-12)

$$\Delta G = (H_{\text{products}} - H_{\text{reactants}}) - T(S_{\text{products}} - S_{\text{reactants}}) \quad (\text{A-15})$$

Since ΔG must be negative for the reaction to proceed, one can see that a system can react due to a high thermal energy base ($H_{\text{reactants}} > H_{\text{products}}$) or a low level of disorder ($S_{\text{reactants}} < S_{\text{products}}$).

In Figure A-1, the free energy expression developed by K. K. Kelley from a National Bureau of Standards circular was used for the thermodynamic analysis presented here. This expression was selected because it falls in the middle of the range of available values presented in Figure A-1. Dr. Ando's expressions had the highest equilibrium constant values for ammonium bisulfate and the lowest for ammonium sulfate. Scott and Cattell's expressions are at the other extreme (i.e., the highest K for $(\text{NH}_4)_2\text{SO}_4$ and the lowest K for NH_4HSO_4). The fact that the other thermodynamic data were at two opposite extremes also influenced the selection of Kelley's values as the data for this analysis.

To begin thermodynamic calculations, some assumptions were necessary. First, the gaseous components were assumed to behave as ideal gases because of the system's relatively low pressure and high temperature. Calculations were performed on all the gaseous components of the system to check this assumption.¹² The following calculation is an example.



Critical temperature, $T_c = 406^\circ\text{K}$

Critical pressure, $P_c = 111 \text{ atm}$

Accentric factor, $\omega = 0.250$

For system @ $T = 500^\circ\text{K}$ (227°C)

$P = 1 \text{ atm}$

$$P_r = \frac{P}{P_c} = 0.00901$$

$$T_r = \frac{T}{T_c} = 1.23$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} = -0.219$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} = 0.0676$$

where B^0 and B^1 are parameters for a generalized correlation of the second virial coefficient in the equation of state for a non-ideal gas.

$$\ln \phi = \frac{P_r}{T_r} (B^0 + \omega B^1) = \frac{.00901}{1.23} [-0.219 + (0.250)(0.0676)] = -0.00148$$

$$\phi = 0.999$$

where, ϕ = fugacity coefficient

The fugacity coefficient, ϕ , describes the non-ideal behavior of a gas in a mixture. For ideal gases, the contribution of a component to any molar thermodynamic property of the mixture (*i.e.*, P , V , H) is equal to the product of the components mole fraction in the mixture and the value of the property for the pure component. For non-ideal gases, the contribution of a component is equal to the product of its mole fraction in the mixture, the value of the property for the pure component, and the fugacity coefficient. For this analysis, all the fugacity coefficients calculated were approximately 1, so the assumption of an ideal gas is valid.

Another assumption made was that reaction products were formed as pure, separate condensed phases. This assumption was made because there were no data available on activity coefficients, γ_i , for ammonium bisulfate and ammonium sulfate in a mixture. (Activity coefficients for liquids and/or solids in mixtures are analogous to fugacity coefficients for gas mixtures.) This assumption does inject a small degree of uncertainty into the analysis since evidence indicates that $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 can form non-ideal solutions. In order to estimate the possible impact of non-ideal solutions

on the analysis, calculations were performed in which the activity coefficient was decreased by a factor of 10. The results of these calculations showed that a large change in the activity resulted in a relatively small change in formation temperature.

There are additional requirements for chemical reaction equilibrium besides constant temperature and constant pressure. Reactions proceed in a direction which causes a decrease in free energy. Therefore, the equilibrium state of a system is that state for which the total free energy is a minimum with respect to all possible changes (i.e., chemical reaction and mass transfer between phases) at a given temperature and pressure.¹³ This criterion for equilibrium can be used to predict equilibrium compositions in a system.

Radian has developed a computer program which estimates the equilibrium composition of a system based on the principle of free energy minimization. The advantage of the free energy minimization methodology is its applicability to complex chemical systems without requiring the specification of reaction mechanisms. In this case it is advantageous since it permits simultaneous consideration of the equilibria between $\text{NH}_3\text{-SO}_3$ and $\text{SO}_3\text{-H}_2\text{O}$.

The free energy minimization procedure is mathematically oriented with emphasis on compounds and their elemental compositions. A brief discussion is presented here to provide a basic understanding of the procedure. The free energy of the system can be written in the following manner.

$$G = \sum_{i=1}^{i=n} \mu_i Z_i \quad (\text{A-16})$$

where, G = Free energy of the system,

n = Number of compounds in system,

μ_i = Chemical potential of i^{th} compound,

Z_i = Number of moles of i^{th} compound.

The chemical potential is given by the following expressions.

$$\mu_i = G_i^\circ \quad (\text{pure phase}) \quad (\text{A-17a})$$

$$\mu_i = G_i^\circ + RT \ln P + \ln \frac{Z_i}{\bar{Z}} \quad (\text{ideal gas}) \quad (\text{A-17b})$$

where, G_i° = Standard free energy of formation for i^{th} compound,

T = System temperature,

P = System pressure,

Z_i = Number of moles of i^{th} compound,

$$\bar{Z} = \sum_{i=1}^n Z_i$$

The other equality that must be satisfied along with the minimization of equation A-16 is a material balance on the elements comprising the compounds in the system.

$$b_j = \sum_{i=1}^n a_{ij} Z_i \quad (\text{A-18})$$

where, b_j = Total number of gram-atoms of element j in system

a_{ij} = Number of atoms of element j in compound i ,

Z_i = Number of moles of i^{th} compound.

The computer program substitutes the appropriate expression of equation A-17 into equation A-16. Then, it minimizes the system's free energy by differentiating equation A-16 and setting the derivatives equal to zero. That expression is solved in terms of Z_i and the resulting expression is substituted into the material balance equation whose solution gives the actual numerical values for each compound's mole number, Z_i .¹⁴

RESULTS OF THE THERMODYNAMIC ANALYSIS

The cases examined for the thermodynamic analysis of this study include all combinations of the following air preheater inlet flue gas concentrations.

<u>NH₃</u>	<u>SO₃</u>	<u>H₂O</u>
10 ppm	5 ppm	10%
30 ppm	10 ppm	
50 ppm	50 ppm	
100 ppm		

The cases were selected primarily to reflect flue gas concentrations that could be encountered at the air preheater inlet, downstream of a NO_x SCR system. Ten ppm NH₃ is a reactor outlet concentration that might be expected from a typical SCR system operating as designed at 80-90 percent NO_x reduction. Thirty ppm NH₃ is a concentration that could result from a system designed for a smaller catalyst charge and/or larger NH₃/NO_x injection ratios. This level of ammonia in the SCR reactor outlet might also occur during a sudden load decrease on the boiler which could result in a temporary increase in flue gas ammonia concentration before the process control equipment can respond. The 50 and 100 ppm NH₃ cases were included to demonstrate the effect of a large excess of ammonia on the system's thermodynamics.

The SO₃ concentrations of 5 and 10 ppm were selected to represent typical coal and low sulfur oil flue gas SO₃ concentrations. The 50 ppm SO₃ case was included to provide an upper limit for SO₃ concentrations that might result from burning a high sulfur fuel oil and to show the effect of a large excess of SO₃. The H₂O concentration in the flue gas was assumed to be 10 percent as this value is typical. For one NH₃/SO₃ combination, cases were evaluated at H₂O concentrations of 5 percent and 15 percent in the flue gas to check the influence of water vapor on the equilibrium concentrations. There was no change in formation temperatures with change in H₂O concentration.

The results of the thermodynamic analysis are shown in Figures A-2 through A-9. Figures A-2, A-3, and A-4 show the effect of changing inlet NH_3 concentration at constant inlet SO_3 concentrations of 5, 10, and 50 ppm, respectively. The equilibrium program predicted that if ammonium sulfate is a potential condensed species of the system, no ammonium bisulfate will form (i.e., ammonium sulfate is the favored species thermodynamically). Therefore, the curves shown in the figures for ammonium bisulfate formation were obtained by specifying bisulfate as the only potential condensed species.

Figures A-2, A-3, and A-4 are plots of the fractional extent of reaction, E , versus temperature. Fractional extent of reaction is defined here as the fraction of the stoichiometrically limiting species that has reacted, for a given temperature and inlet NH_3/SO_3 concentrations. More specifically,

<u>$\text{NH}_3:\text{SO}_3$ Ratio</u>		<u>E</u>
<u>Bisulfate formation</u>	<u>Sulfate formation</u>	
> 1	> 2	$\frac{Y_{\text{SO}_3}^i - Y_{\text{SO}_3}^f}{Y_{\text{SO}_3}^i}$
< 1	< 2	$\frac{Y_{\text{NH}_3}^i - Y_{\text{NH}_3}^f}{Y_{\text{NH}_3}^i}$

where: i = initial

f = final

As shown in Figures A-2, A-3, and A-4, the initial product formation temperature increases with increasing NH_3 concentrations although the rate of increase declines. This phenomenon is shown more vividly in Figure A-5 where the initial product formation temperature is plotted versus inlet NH_3 concentration. The cases for NH_3 concentrations that are more likely to occur in

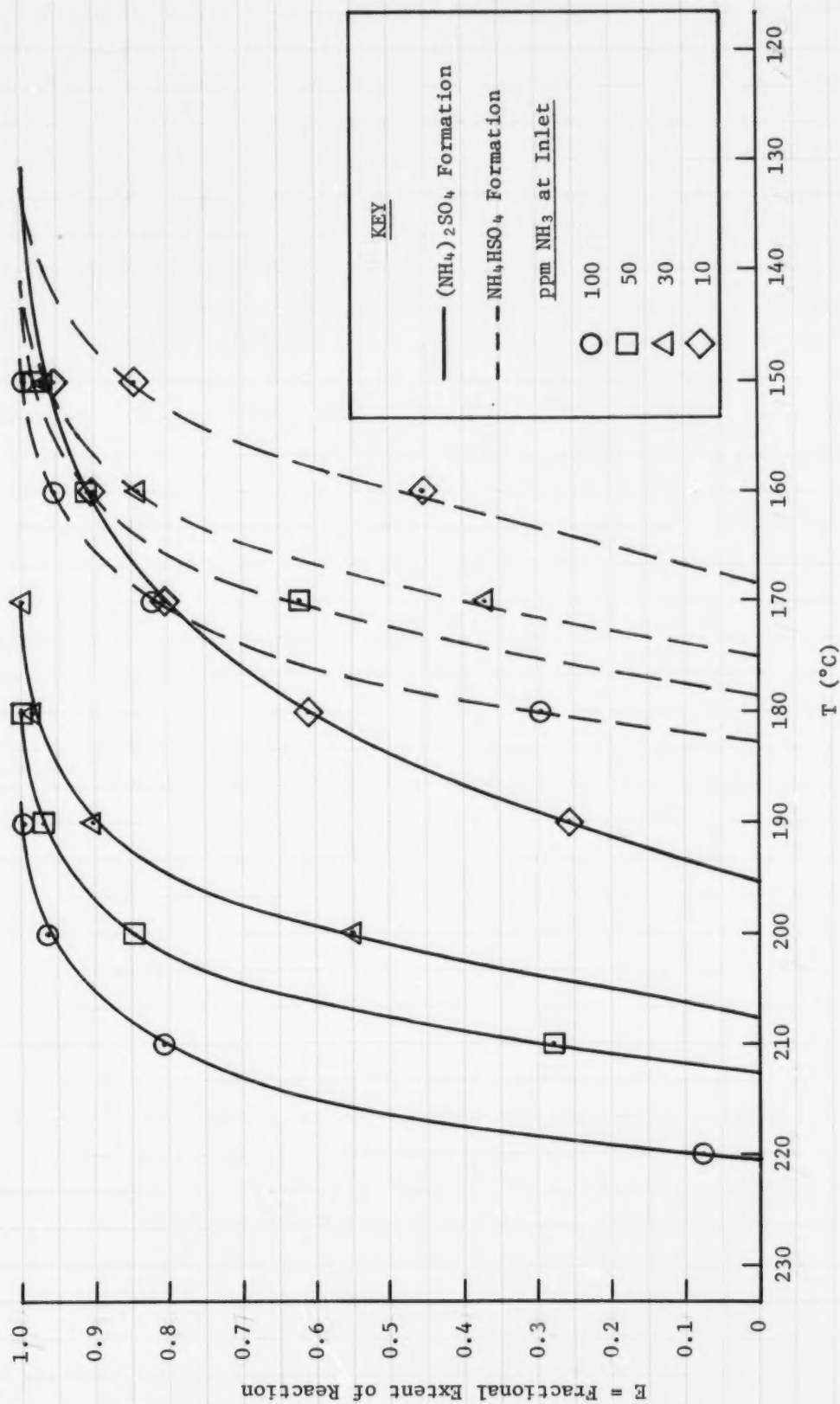


Figure A-2. Thermodynamic equilibria for ammonium sulfate and ammonium bisulfate with 5 ppm SO₃ at inlet.

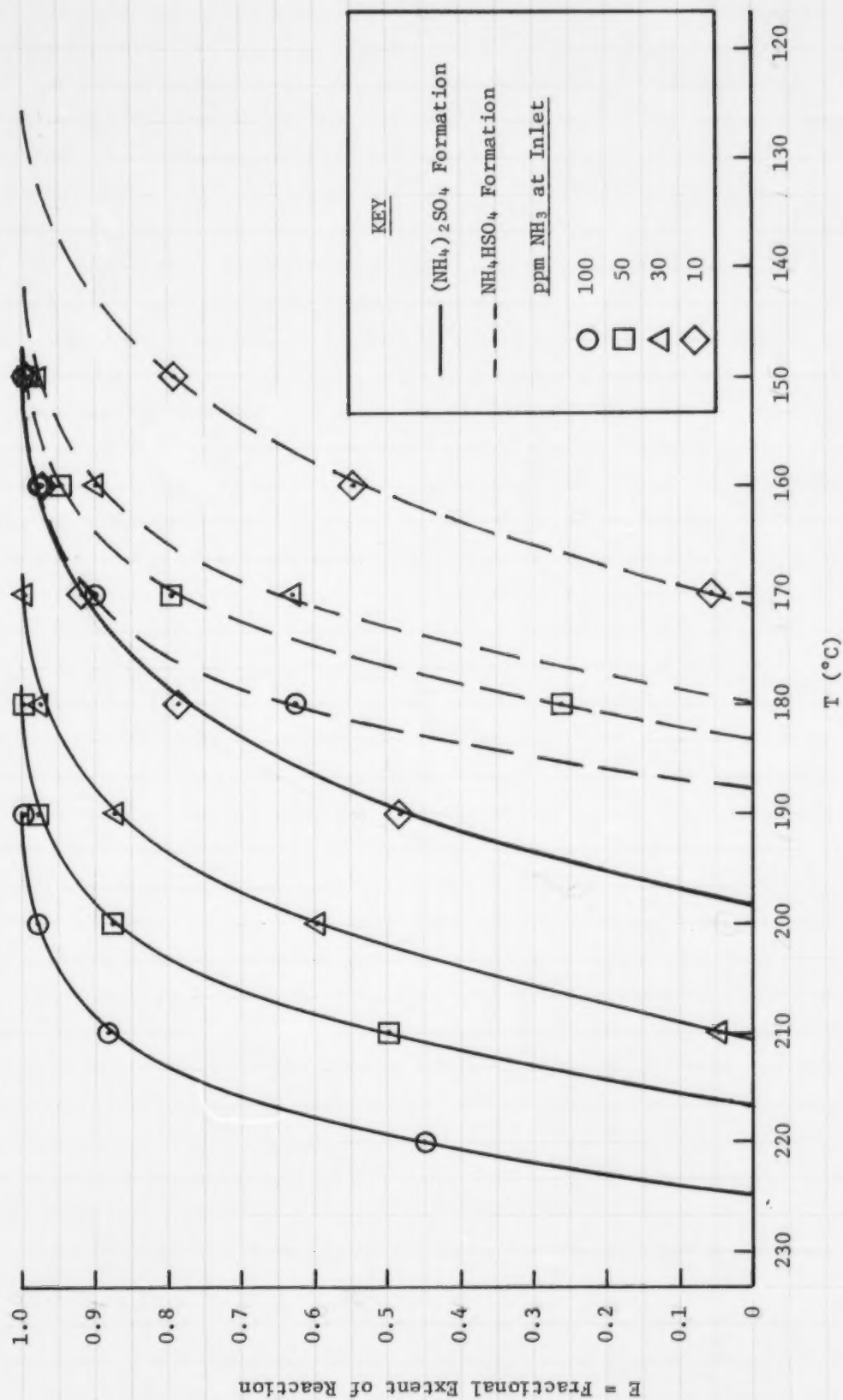


Figure A-3. Thermodynamic equilibria for ammonium sulfate and ammonium bisulfate with 10 ppm SO₃ at inlet.

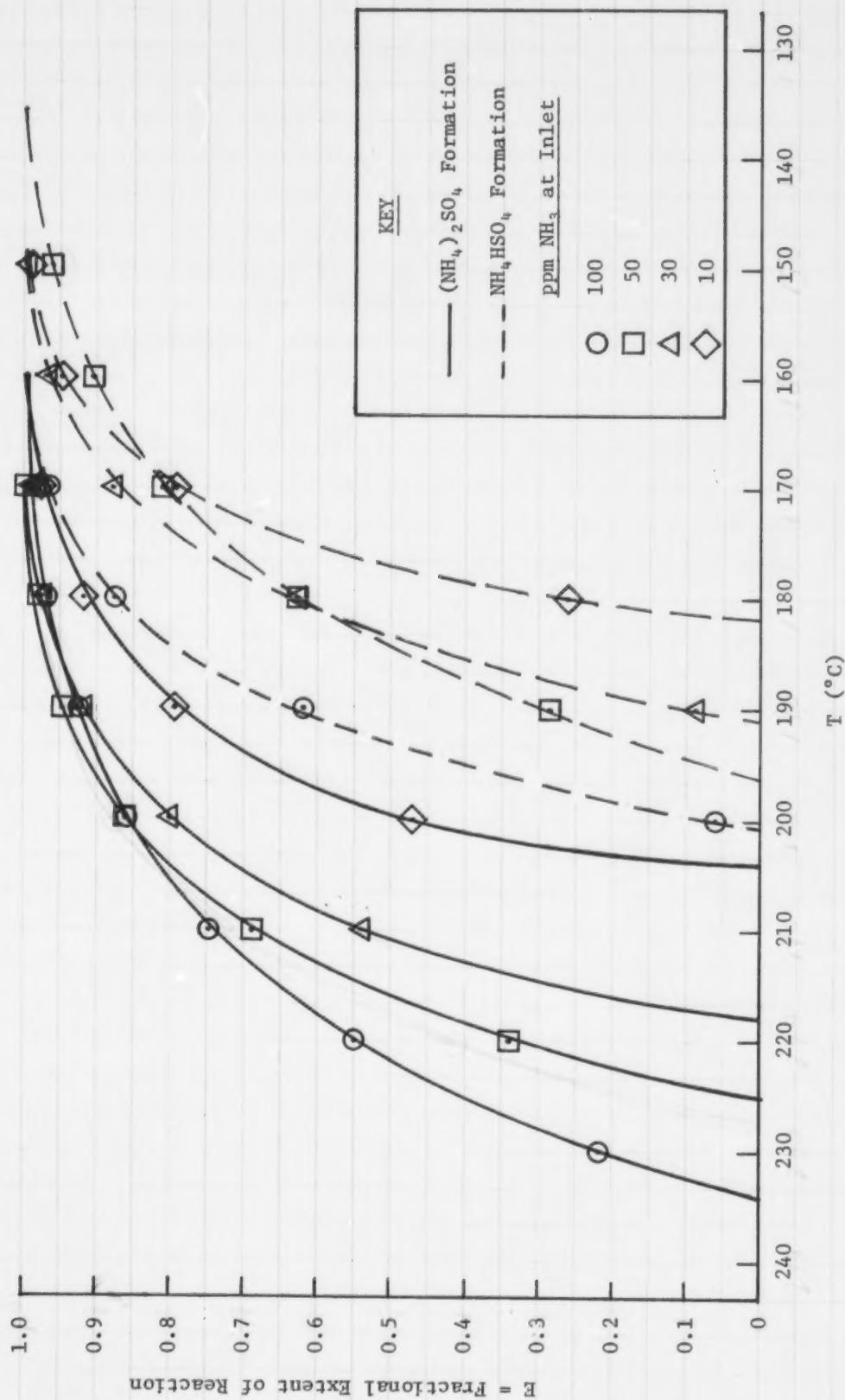


Figure A-4. Thermodynamic equilibria for ammonium sulfate and ammonium bisulfate with 50 ppm SO_3 at inlet.

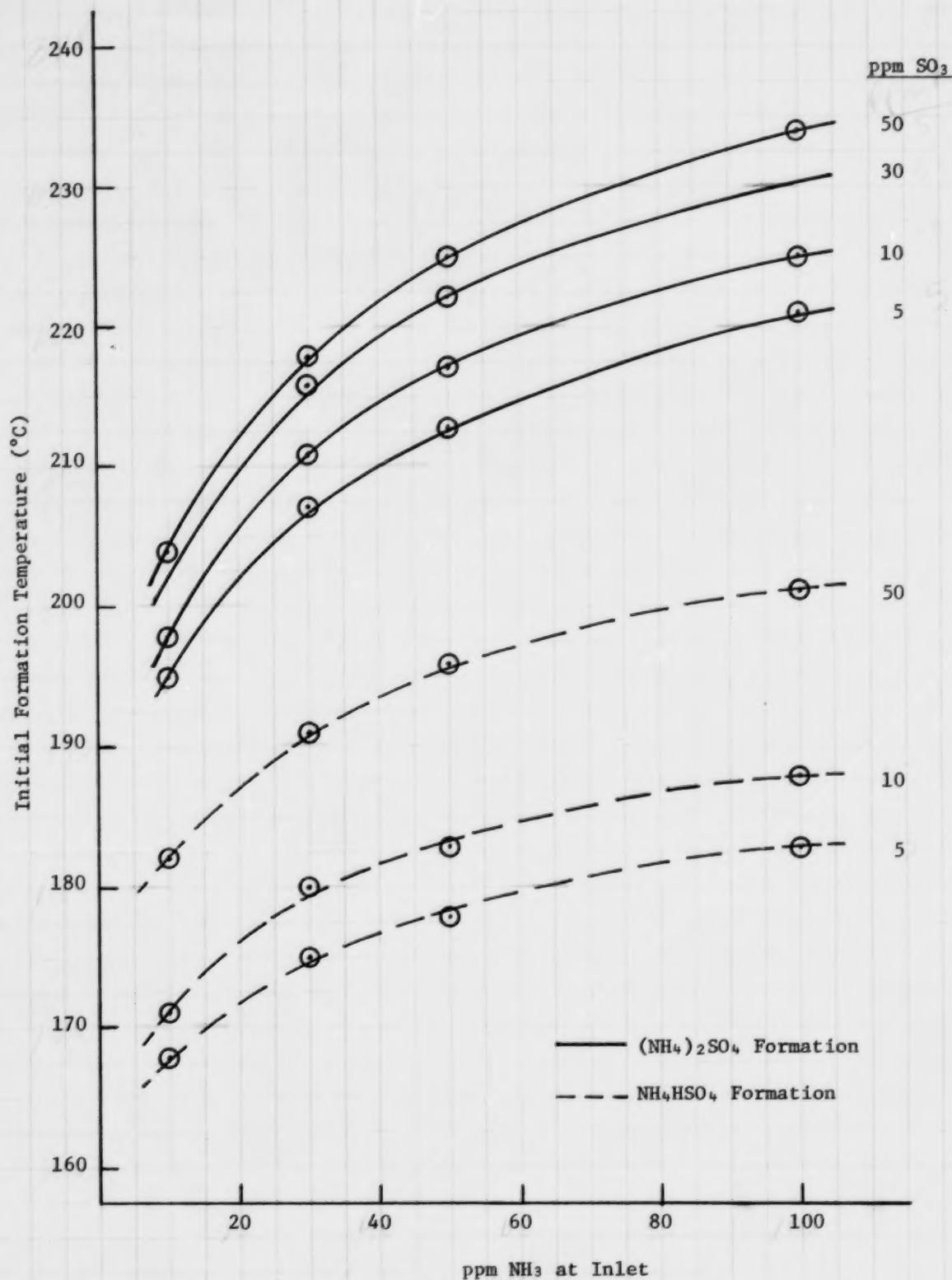


Figure A-5. Initial product formation temperature as a function of NH₃ at inlet.

an actual SCR application (10 and 30 ppm NH_3) are shown in Figures A-6 and A-7. Each of these figures shows that increasing inlet SO_3 concentration raises the initial product formation temperature. This effect is shown more clearly in Figure A-8 where initial formation temperature is plotted versus inlet SO_3 concentration.

These figures show that increasing the NH_3 concentration has a greater effect on the sulfate formation temperatures while an increase in SO_3 concentration has a greater impact on the bisulfate formation temperatures. Examination of the equilibrium constants for the sulfate and bisulfate reactions (equations A-19 and A-20) reveals the reason for this behavior.

$$K_{(\text{NH}_4)_2\text{SO}_4} = \frac{a_{(\text{NH}_4)_2\text{SO}_4}}{[\text{NH}_3]^2 [\text{SO}_3] [\text{H}_2\text{O}]} \quad (\text{A-19})$$

$$K_{\text{NH}_4\text{HSO}_4} = \frac{a_{\text{NH}_4\text{HSO}_4}}{[\text{NH}_3] [\text{SO}_3] [\text{H}_2\text{O}]} \quad (\text{A-20})$$

For constant SO_3 and H_2O concentrations, a change in NH_3 concentration will have a larger impact on the $(\text{NH}_4)_2\text{SO}_4$ equilibrium constant since the NH_3 concentration appears as a squared term. On the other hand, a change in SO_3 concentration has a greater impact on the NH_4HSO_4 equilibrium constant since it represents a larger fraction of the denominator in equation A-20 than in equation A-19.

From Figures A-6, A-7, and A-8, it appears that formation of ammonium sulfates should begin to occur at 200-220°C for most potential flue gas conditions. In terms of air preheater operation, this means that deposits will begin to form in the intermediate temperature zone.

In Figures A-2, A-3, A-4, A-6, and A-7, the individual curves do not all have the same slope. The bisulfate cases for 10 ppm NH_3 /10 ppm SO_3 and 50 ppm NH_3 /50 ppm SO_3 and the sulfate cases for 10 ppm NH_3 /5 ppm SO_3 and 100 ppm NH_3 /50 ppm SO_3 have the smallest slopes. In other words, for the above

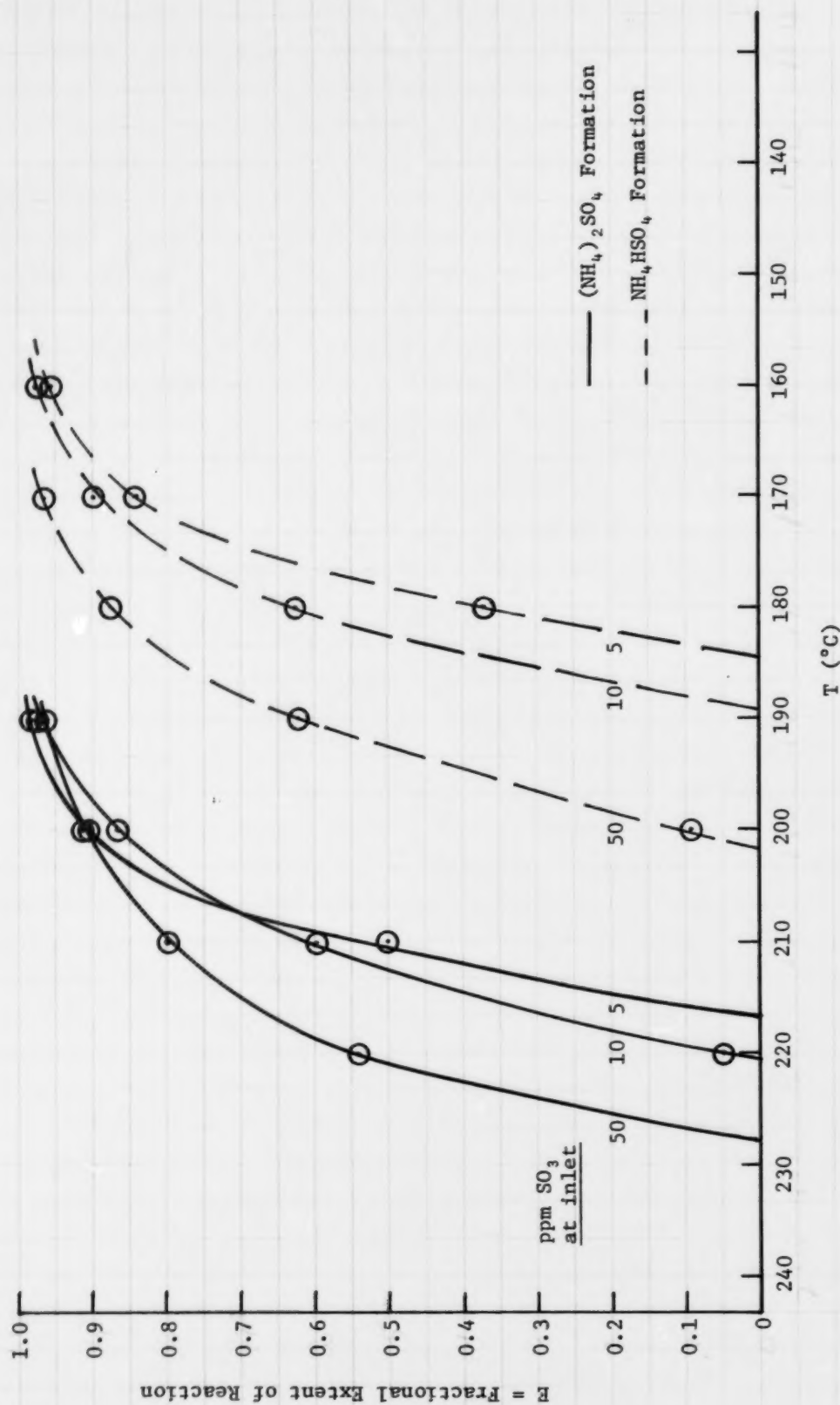


Figure A-7. Thermodynamic equilibria for ammonium sulfate and ammonium bisulfate with 30 ppm NH_3 at inlet.

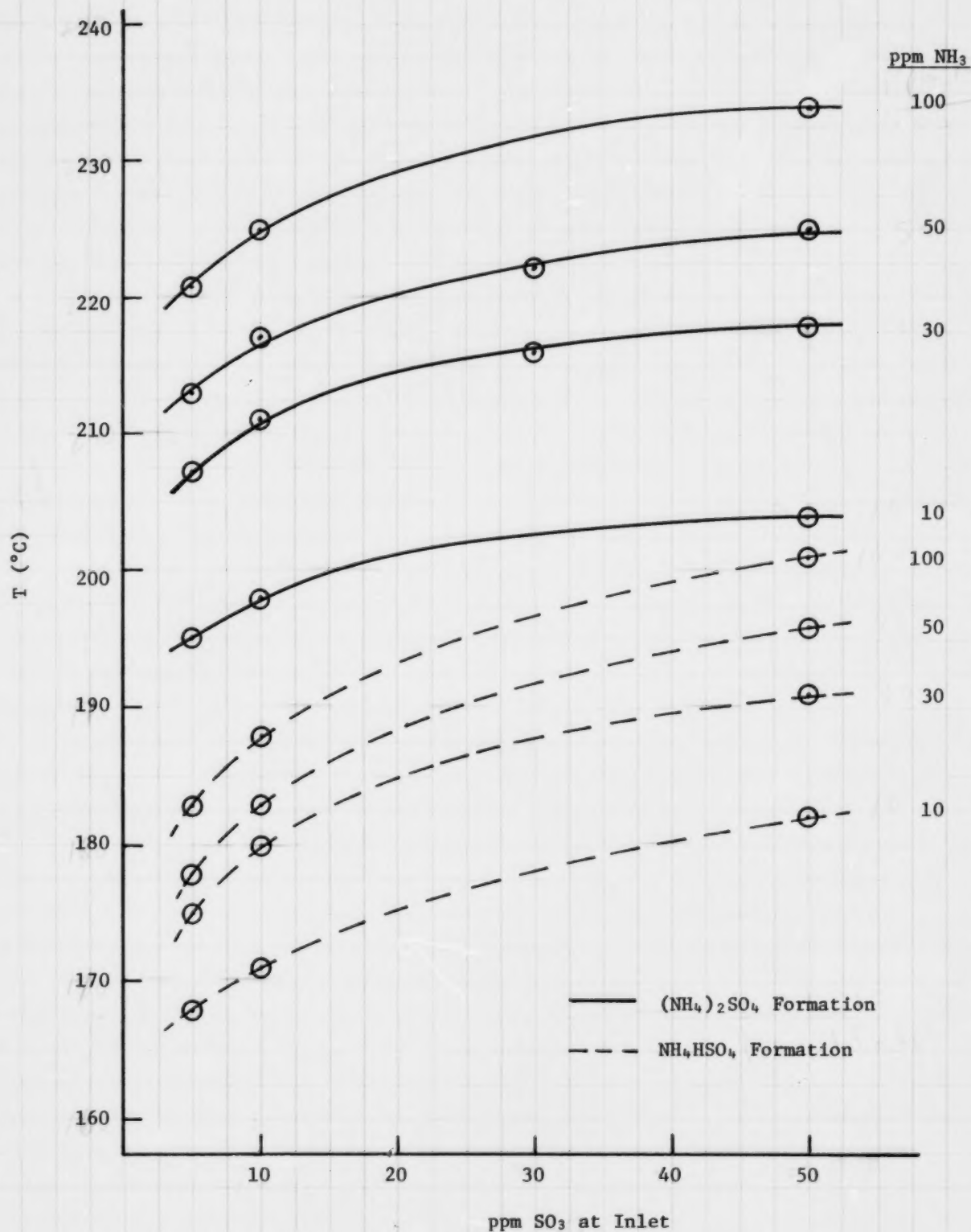


Figure A-8. Initial product formation temperature as a function of SO_3 at inlet.

cases it takes a larger temperature drop to send the reactions to the same degree of completion. Without either gaseous reactant being in excess of the stoichiometric concentration (as in the above cases), there is less of a driving force for the formation reactions to go to completion. This behavior can be explained by examining Equations A-19 and A-20. For a given value of the equilibrium constant, K , an increase in flue gas NH_3 concentration will result in a reduction in the equilibrium SO_3 concentration. If the NH_3 concentration is increased enough, the equilibrium SO_3 concentration will be very small and the formation reactions will be essentially complete.

Figure A-9 shows the temperature drop required for the formation reactions to proceed to 95 percent completion as a function of the inlet NH_3/SO_3 mole ratio. All the cases evaluated in this study are represented in Figure A-9. The curves drawn are approximate; depending on actual gas concentrations, ΔT_{95} will fall above or below the curve by a few degrees. The curves do show, however, the effect of moving further away from the stoichiometric ratio, that of decreasing the temperature drop required for complete reaction. One can see that most of the temperature drops required for 95 percent reaction are in the range of 30-50°C. For 90 percent reaction, most of the values are around 30°C and most of the temperature drops required for 80 percent reaction are about 20°C. This is significant in terms of air preheater operation. It means that most deposition could be limited to a small region of the preheater. While Japanese experience has not shown evidence of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposition being confined to a narrow region, it may be possible to modify air preheater design so this occurs.

Another significant result of Radian's thermodynamic analysis is that the predicted formation temperatures for $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 were lower than those predicted by investigators in Japan. It appears that previous investigators' thermodynamic analyses of these reactions neglected to include the sulfuric acid formation reaction. (Besides Dr. Ando, most of the studies in this area have been conducted by developers of SCR processes.)

ΔT_{95} = Temperature Drop Required for 95% Extent of Reaction, °C

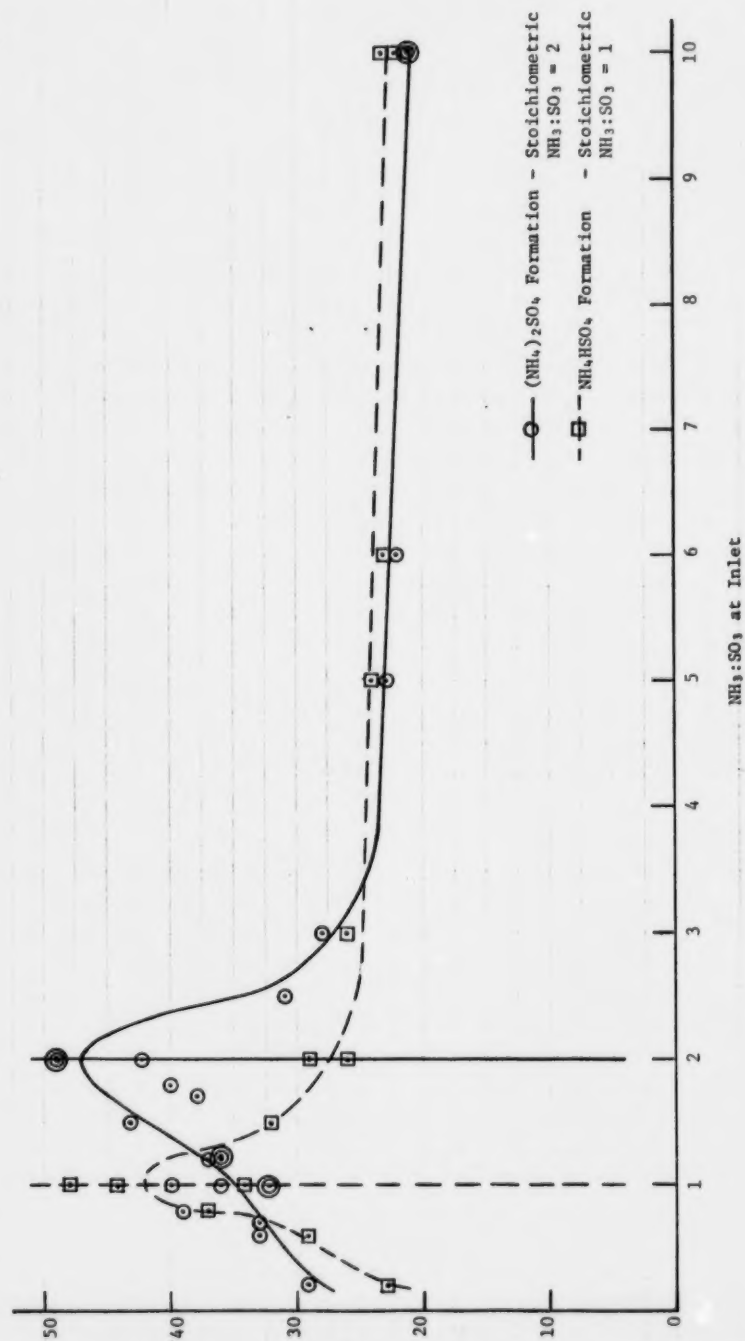


Figure A-9. Temperature drop required for 95 percent extent of reaction as a function of inlet NH₃:SO₃.

In the temperature range of product formation, over 90 percent of the SO_3 that was present at the inlet of the air preheater has been converted to H_2SO_4 vapor. This tends to lower the product formation temperatures since there is effectively less SO_3 available for reaction. Also, the formation reactions involving H_2SO_4 occur at lower temperatures due to the smaller free energy change associated with these reactions. This is shown graphically in Figure A-10 on the following page. Radian's predicted initial formation temperatures are $\sim 40^\circ\text{C}$ less for ammonium bisulfate and $\sim 20^\circ\text{C}$ less for ammonium sulfate than those of the other authors.

Lower standard free energies for the reactants will decrease the equilibrium constant of the formation reactions. Since the bisulfate formation reaction has a smaller equilibrium constant (see Figure A-1), a decrease in the free energy of the reactants will have a greater effect on it than the equilibrium constant for sulfate formation. The effect of H_2SO_4 on the product formation temperatures diminishes with increasing system temperature; higher temperatures favor the decomposition of H_2SO_4 to SO_3 and H_2O .

COMPARISON WITH DR. ANDO'S EXPERIMENTAL RESULTS

Dr. Ando performed a number of laboratory experiments on the formation of ammonium bisulfate and ammonium sulfate. The equipment in which these chemical reactions occurred was a series of glass tubes, connected by U-joints, immersed in a constant temperature oil bath. The gaseous reactants, NH_3 and H_2SO_4 vapor, were mixed together and passed through an electric furnace to guarantee all products will form in the glass tubes. The gas cools as it passes through the tubes and ammonium bisulfate and/or ammonium sulfate begin(s) to form.

Figure A-11 shows the fractional extent of reaction as a function of temperature for Radian's equilibrium calculations and for Dr. Ando's experimental results. These results are for a case with 200 ppm NH_3 , 200 ppm SO_3 , and 10 percent H_2O at the inlet. One can see that the predicted initial

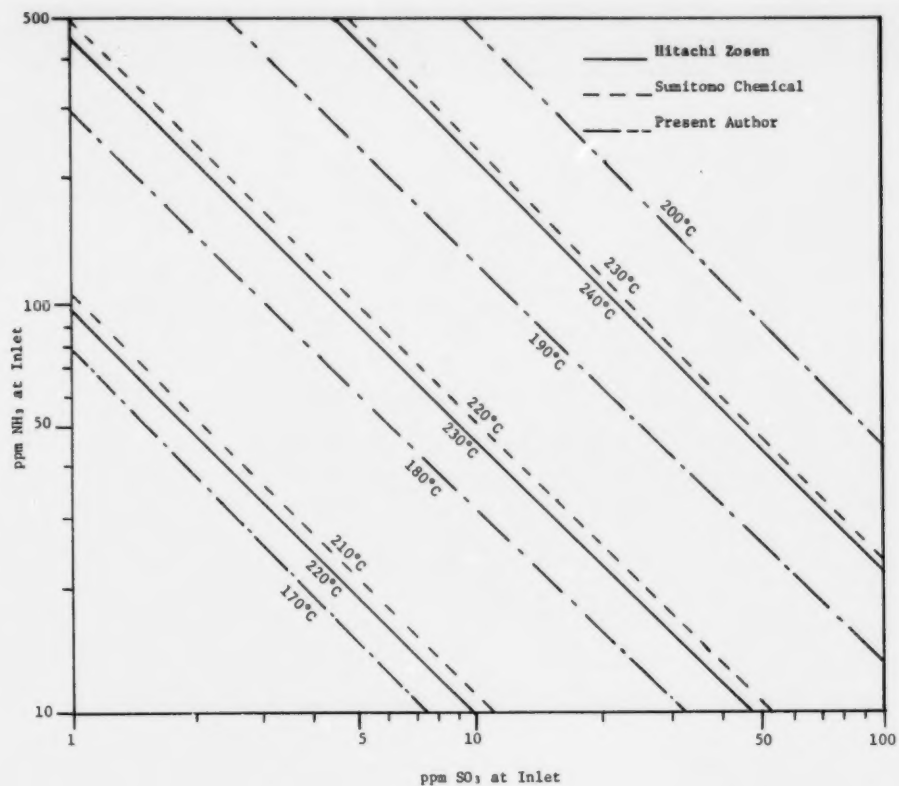


Figure 10-a. NH_4HSO_4 initial formation temperature.

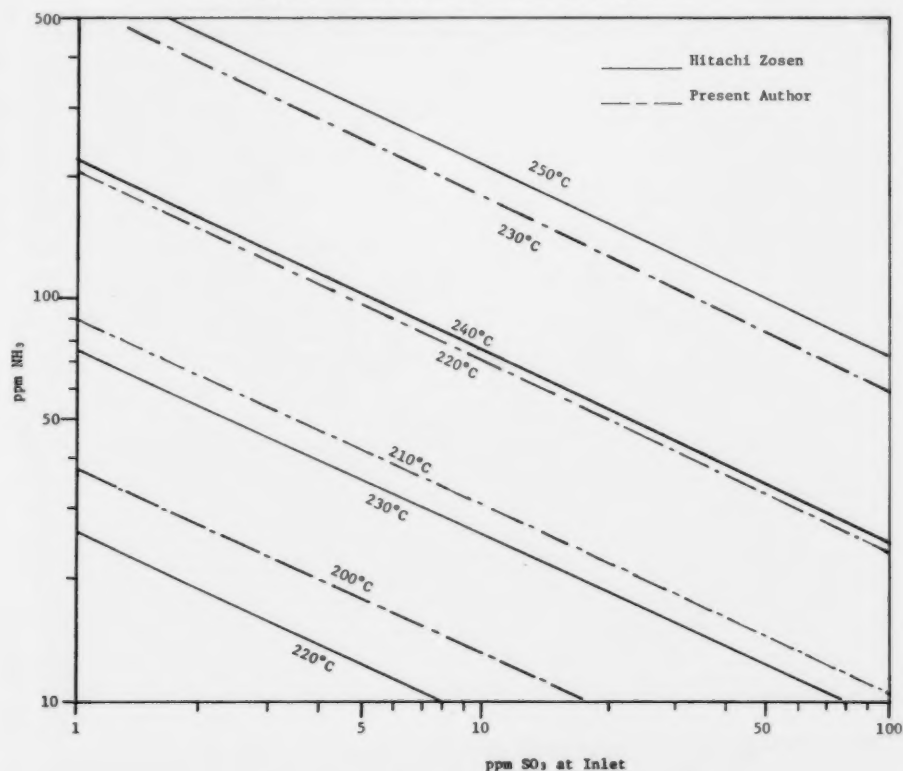


Figure 10-b. $(\text{NH}_4)_2\text{SO}_4$ initial formation temperature.

Figure A-10. Theoretical prediction of initial formation temperatures for ammonium bisulfate and ammonium sulfate.^{15,16}

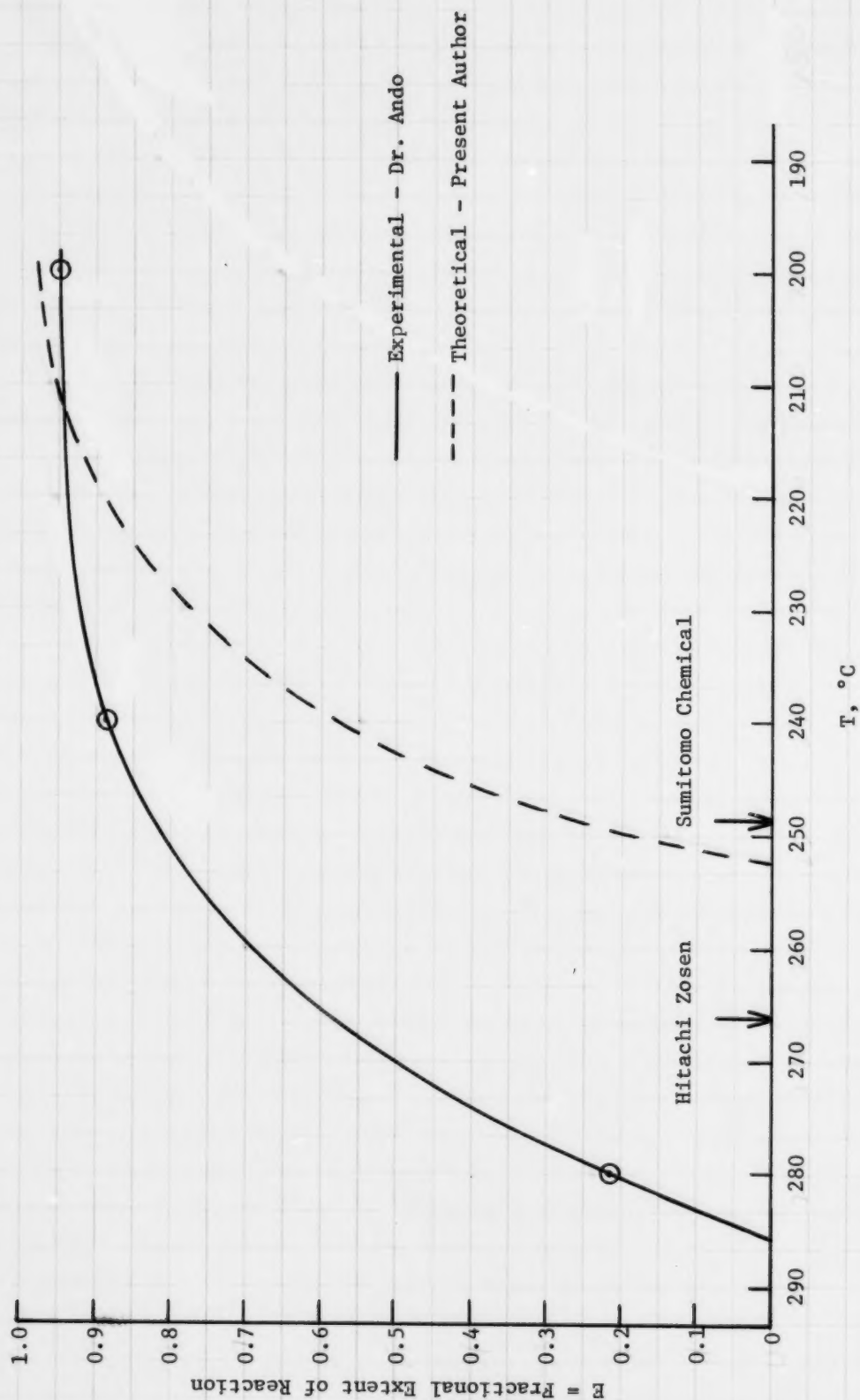


Figure A-11. Comparison of theoretical vs. experimental thermodynamic equilibria for case with 200 ppm NH_3 and 200 ppm SO_3 at inlet.

product formation temperature, 255°C, is well below the 280°C tests which Dr. Ando performed and did find deposits. It appears from Dr. Ando's report and a conversation with him that he did not analyze those deposits from the high temperature tests (the 280°C point on the plot is an average value of 2 tests). In a subsequent communication, Dr. Ando did indicate that a section of the apparatus was exposed to air and he believed these deposits formed in that section. Some other possible explanations for the fact that Dr. Ando had deposits form at a temperature 20-30°C above our predicted initial formation temperatures are:

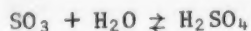
- Incorrect thermodynamic information,
- Undetermined (not analyzed) reaction product formed other than ammonium sulfate or ammonium bisulfate,
- Higher reactant concentrations due to malfunctioning gas flow meters (either NH_3 or dilution air),
- Errant oil bath temperature readings due to poor bath agitation or placement of the thermometer too near heating coils.

There is close agreement on thermodynamic properties among various sources. (Dr. Ando's thermodynamic expressions give 263°C as the initial formation temperature for this case). Since no available information suggests the formation of other products, it appears that some experiemntal error is the principal reason for the discrepancy between our results and Dr. Ando's. Additional laboratory investigation of the thermodynamics and kinetics of the system is required to resolve this discrepancy.

In summary, calculations were performed to determine what conditions of temperature and concentrations lead to formation of ammonium sulfates. They estimate the type and amount of compounds formed as the flue gas is cooled. The most significant results of this work are:

- For most expected flue gas conditions, solids formation should begin to occur at 200-220°C,

- Approximately 80 percent of the NH_3 and SO_3 will react in a narrow (20°C) temperature range and >90 percent should react within 30°C (unless NH_3/SO_3 mole ratio is close to stoichiometric).
- Previously reported formation temperatures appear to be high due to neglecting the following reaction:



which effectively lowers the SO_3 concentration.

- $(\text{NH}_4)_2\text{SO}_4$ is the most stable product thermodynamically and the formation of NH_4HSO_4 would have to be the result of favorable reaction kinetics.

APPENDIX A
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APPENDIX B

KINETIC ANALYSIS OF $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ FORMATION AND DEPOSITION

INTRODUCTION

The deposition of ammonium sulfate compounds on heat transfer surfaces falls into the general classification of simultaneous heat and mass transfer problems. Previous work in this area has focused on a similar problem which involves condensation of a liquid from a gas stream. However, the deposition of NH_3 and SO_3 (or H_2SO_4 vapor) reaction products is a more complex one than that typically treated in the literature. First, NH_3 and SO_3 (H_2SO_4) undergo chemical reaction as opposed to condensation. Second, the compounds formed are not well defined. Several possible reaction products can be present in the deposits which form on the heat transfer surface.

Flue gas temperature downstream of an SCR process is about 400°C . It contains H_2O , SO_3 , residual NH_3 , and other species. As the flue gas is cooled, the SO_3 and H_2O react to form vapor phase H_2SO_4 . Upon further cooling, the NH_3 and H_2SO_4 react to form condensate products on the heat exchange surface and aerosol products in the bulk gas. Some of the aerosol will remain in the bulk gas and some is deposited on the heat transfer surface. One assumption that is normally made in the design of partial condensers is that any aerosol formed is in equilibrium with the vapor in immediate contact with it. This assumption eliminates the possibility of supersaturation of the bulk gas, thus lowering the potential concentration driving force for diffusion mass transfer to the surface. This could lower the amount of predicted deposits relative to observed deposits.

In an effort to identify the factors which control $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ deposit formation, a model was developed. This model was designed to estimate the amount of deposit formation in a heat exchanger by considering the rates of heat and mass transfer. The chemical reaction rate was assumed to be rapid relative to the heat and mass transfer rates and therefore, was neglected. The principal reason for this assumption was that available data indicated the chemical reaction occurs almost instantaneously at low temperatures.¹ The validity of this assumption will be evident when the model is applied to experimental data.

Modeling the deposition of compounds from the chemical reaction of NH_3 and SO_3 in flue gas has several aspects which must be considered. First, thermodynamic calculations are required to estimate the temperature range in which deposits will form and to determine the driving force for mass transfer. Second, a description of the heat transfer characteristics of the system is required. Mass transfer calculations may then be made and the quantity of deposits estimated. This is an iterative process. Comparison of experimental results with computed theoretical results will probably indicate a need for a revised computational procedure and/or additional data.

There are basically four distinct, yet interrelated, physical phenomena of importance to a model of the deposition of ammonium sulfate compounds on heat transfer surfaces. These are:

- chemical reaction thermodynamics
- heat transfer
- mass transfer
- chemical reaction kinetics

As discussed above, the chemical reaction rate is assumed to be rapid with respect to the rates of heat and mass transfer and will not be included in developing the model. The role of each of the other factors is discussed next.

TECHNICAL APPROACH

Chemical Reaction Thermodynamics

Thermodynamic equilibrium calculations were made for a gas phase and two pure condensed phases. The individual species considered are listed in Table B-1 below.

TABLE B-1. SPECIES CONSIDERED

Gas		Liquid	Solid
NH ₃	N ₂	NH ₄ HSO ₄	(NH ₄) ₂ SO ₄
SO ₃	H ₂ SO ₄		
H ₂ O			

(The assumptions, procedures, and results of the thermodynamic analysis are presented and discussed in Appendix A.) The results of the calculations show that sulfur is present predominately as sulfuric acid vapor and not as SO₃. Also, (NH₄)₂SO₄ appears to be a more stable product than NH₄HSO₄ (i.e., its formation is favored thermodynamically).

An expression for the equilibrium constant as a function of temperature was obtained for each reaction. Knowing the expression for the equilibrium constant allows the calculation of the equilibrium concentrations in the gas film and in the bulk gas.

Heat Transfer

Simultaneous heat and mass transfer are normally modeled as transport through a boundary layer (or film) between a completely mixed bulk gas and the heat transfer surface. The rapidity of heat transfer is determined by the bulk gas properties, such as thermal conductivity.

Thermal conductivity describes the ability of a substance to conduct heat. For gases, thermal conductivity is determined primarily by movements of and collisions between molecules. (This is, to a first approximation, determined by the bulk gas molecular weight.)

Because the concentrations of NH_3 and SO_3 in the flue gas will not significantly change the bulk properties of the flue gas, the heat transfer rate is not affected by formation of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$. Temperature profiles in a heat exchanger may be calculated directly from the streams' inlet and outlet temperatures and the exchanger's dimensions. A simplified energy balance is given in Equation B-1.²

$$G C_p dt + q dA = 0 \quad (\text{B-1})$$

where: G = mass flow of gas, g-moles/sec

C_p = heat capacity of gas, cal/g-mole $\cdot^\circ\text{K}$

dt = differential temperature change of gas, $^\circ\text{K}$

q = heat flux, cal/cm²·sec

dA = differential heat transfer surface area, cm²

The value of the heat flux, q , may be calculated from film or overall considerations.³

$$\text{Film heat transfer} \quad q = h_i(t - t_i) \quad (\text{B-2a})$$

or

$$\text{Overall heat transfer} \quad q = U(t - t_c) \quad (\text{B-2b})$$

where: q = heat flux, cal/cm²·sec

h_i = gas film heat transfer coefficient, cal/cm²·sec $\cdot^\circ\text{K}$

t = bulk gas temperature, $^\circ\text{K}$

t_i = interface temperature, $^\circ\text{K}$

U = overall heat transfer coefficient, cal/cm²·sec $\cdot^\circ\text{K}$

t_c = coolant temperature, $^\circ\text{K}$

From Equation B-2b, the local heat transfer is defined.

$$dQ = U_{\ell} (t - t_c) dA \quad (B-3)$$

where: dQ = heat transfer in area increment dA , cal/sec

U_{ℓ} = local overall heat transfer coefficient, cal/cm²·sec·°K

t_c = coolant temperature, °K

dA = differential area increment, cm²

This equation may be integrated over the total area of the heat exchanger by assuming an average overall heat transfer coefficient, U_a and an average temperature difference ΔT_a .

$$Q = U_a \cdot \Delta T_a \cdot A \quad (B-4a)$$

$$U_a = Q / \Delta T_a \cdot A \quad (B-4b)$$

Values of U_a may be calculated from experimental data. Q is calculated from the inlet and outlet temperatures, the heat capacity of the gas, and the flow rate using the following equation.

$$Q = GC_p (T_{in} - T_{out}) \quad (B-5)$$

where: Q = heat transfer rate, cal/sec

T_{in} = inlet gas temperature, °K

T_{out} = outlet gas temperature, °K

The area of the heat exchanger, A , is calculated from the dimensions of the exchanger and ΔT_a is calculated from the log mean ΔT formula:

$$T_{LM} = \frac{\Delta T_2 - \Delta T_1}{\ln(\Delta T_2 / \Delta T_1)} \quad (B-6)$$

where, ΔT_1 and ΔT_2 are the temperature differences between the gas and coolant at the inlet and outlet of the heat exchanger.

The local overall heat transfer coefficient may also be calculated from its component parts.⁴ For a tubular exchanger, the following equations apply.

$$U_{\ell} = \frac{1}{\frac{1}{h_i} + \frac{x_t}{k_t} + \frac{1}{h_o}} \quad (B-7a)$$

$$U_{\ell} = \frac{1}{\frac{1}{h_i} + \frac{1}{\alpha}} \quad (B-7b)$$

where: x_t = tube thickness, cm

k_t = thermal conductivity of tube material, cal/(cm²·sec·°K/cm)

h_o = coolant film heat transfer coefficient, cal/cm²·sec·°K

α = combined tube wall and coolant film heat transfer coefficient, cal/cm²·sec·°K

To determine the local overall heat transfer coefficient, the gas film heat transfer coefficient, h_i , and the combined tube wall and coolant film heat transfer coefficient, α , must first be determined. Wilson proposed a useful graphical method of interpreting heat transfer in surface condensers that is applicable to many heat exchange problems. If a series of tests (three or more) are run on a heat exchanger with the fluid rate varied on one side only (gas or coolant), then the change in the overall coefficient is a function of the change in that film coefficient. With data for three different gas velocities, the combined tube wall and coolant film heat transfer coefficient can be determined from the following equation.⁵

$$\frac{1}{U_a} = \frac{1}{\gamma (Re)^{0.8}} + \frac{1}{\alpha} \quad (B-8)$$

where: γ = empirical constant, $\text{cal}/\text{cm}^2 \cdot \text{sec} \cdot ^\circ\text{K}$
 Re = Reynolds number, dimensionless

Knowing the inlet and outlet gas temperatures, the heat capacity of the gas, the flowrate, and the heat exchanger dimensions, U_a can be calculated from Equation B-4. The Reynolds number is calculated from the gas flowrate, composition, viscosity, and tube diameter.⁶

$$Re = DG_f M/\mu \quad (B-9)$$

where: D = tube inner diameter, cm
 G_f = mass flux of gas, $\text{g-mole}/\text{cm}^2 \cdot \text{sec}$
 M = molecular weight of gas, $\text{g}/\text{g-mole}$
 μ = gas viscosity, $\text{g}/\text{cm} \cdot \text{sec}$

Plotting the inverse of the overall heat transfer coefficient versus the inverse of the Reynolds number raised to the 0.8 power for each of three experiments gives a straight line whose intercept equals $1/\alpha$. (Applying this model to the experimental data in the following section of this appendix, α is assumed constant throughout the length of exchanger. This assumption should be valid as the coolant used in the experiments is a constant temperature oil bath, thus h_o should be approximately constant.

Next, the gas film heat transfer coefficient, h_i , is calculated using the Colburn equation.⁷

$$h_i = .023 C_p G_f \frac{Re^{-0.2}}{\left(\frac{C_p \mu}{k_g}\right)^{2/3}} \quad (B-10)$$

where: k_g = thermal conductivity of gas, $\text{cal}/(\text{cm}^2 \cdot \text{sec} \cdot ^\circ\text{K}/\text{cm})$

Knowing α and h_i , U_ℓ is calculated by Equation B-7b for each area increment of the heat exchanger. Then, Equations B-1 and B-2b are combined to calculate the temperature change of the gas as it passes to the next area increment down the exchanger (Equation B-11).

$$dt = \frac{-U_\ell}{GC} (t - t_c) dA \quad (B-11)$$

The temperature of the gas in the next area increment is equal to the sum of the gas temperature in the previous increment, t , and the temperature change, dt . Bulk gas properties are evaluated at the new temperature and then new values of h_i and U_ℓ are calculated. The gas temperature change to the next area increment is then calculated and the process is repeated through the exchanger to the outlet.

MASS TRANSFER

Once the heat transfer characteristics of the system have been described, the mass transfer of the gaseous components can be determined. The mass transfer rate and hence the deposition of ammonium sulfates, is temperature dependent and therefore dependent on the heat transfer rate.

The mass transfer model is complicated by the fact that the condensing material is the result of a chemical reaction. As a result, the diffusing species are not the condensing species. The diffusivity of the gaseous components is determined by the molecular motion of the diffusing species. Diffusivity, like thermal conductivity, is primarily a function of molecular weight and to some extent, a function of temperature. There is a major difference though. Thermal conductivity is based on the bulk gas. Diffusivity is based on the individual species.

For this analysis two cases are examined, that of a superheated bulk gas and that of a saturated (with respect to NH_3 and H_2SO_4) bulk gas.

Case 1. Condensation From a Superheated Bulk Vapor

For superheated vapors there is no aerosol formed and a decrease in vapor concentration results in condensed products on the surface. The overall material balance simplifies to:

$$-dV_a = \alpha_a NdA \quad (\text{B-12})$$

$$-dV_s = \alpha_s NdA$$

where: V_a = molar flow rate of vapor phase NH_3 , g-moles/sec
 α_a = stoichiometric coefficient of NH_3 (=1 for bisulfate, =2 for sulfate), dimensionless
 N = condensate mass flux, g-moles/cm²·sec
 dA = differential surface area of mass transfer, cm²
 V_s = molar flow rate of vapor phase H_2SO_4 , g-moles/sec
 α_s = stoichiometric coefficient of H_2SO_4 =1, dimensionless

It will be helpful to define a new variable, x , which represents the moles of condensate per mole of flue gas. The material balance can now be expressed by:

$$Gdx = NdA \quad (\text{B-13})$$

where: G = moles of flue gas, g-moles/sec
 dx = change in moles of condensate per mole of flue gas, g-moles condensate/g-moles flue gas

The moles of ammonia, V_a , may be expressed in terms of the mole fraction, y , and the flowrate as may sulfuric acid, V_s .

$$dV_a = G dy_a \quad (\text{B-14a})$$

$$dV_s = G dy_s \quad (\text{B-14b})$$

Equations B-13 and B-14 may be substituted into B-12 and the result integrated.

$$-G dy_a = \alpha_a G dx \quad (\text{B-15a})$$

$$-G dy_s = \alpha_s G dx \quad (\text{B-15b})$$

$$y_a = y_{a,\text{inlet}}^{-\alpha_a x} \quad (\text{B-16a})$$

$$y_s = y_{s,\text{inlet}}^{-\alpha_s x} \quad (\text{B-16b})$$

The mass transfer of condensing material, N_dA , can be expressed as a rate. It has the form of a mass transfer coefficient times a driving force. The rate of condensation may be written in terms of either reactant.⁸

$$G dx = \frac{1}{\alpha_a} k_a P (y_a - y_{ai}) dA \quad (\text{B-17a})$$

$$G dx = \frac{1}{\alpha_s} k_s P (y_s - y_{si}) dA \quad (\text{B-17b})$$

where: k_a = NH_3 mass transfer coefficient, $\text{g-moles/cm}^2 \cdot \text{sec} \cdot \text{atm}$
 P = system pressure, atm
 y_a = bulk gas NH_3 mole fraction
 y_{ai} = interface NH_3 mole fraction
 k_s = H_2SO_4 mass transfer coefficient, $\text{g-moles/cm}^2 \cdot \text{sec} \cdot \text{atm}$
 y_s = bulk gas H_2SO_4 mole fraction
 y_{si} = interface H_2SO_4 mole fraction

The mass transfer coefficient, k_r , for each of the gaseous reactants is defined by:⁹

$$k_r = \frac{h_i}{PC_p} \left(\frac{C_{p,r} B_r \rho}{k_g} \right)^{2/3} \quad (\text{B-18})$$

where: k_r = mass transfer coefficient of gaseous reactant r ,
g-moles/cm²·sec·atm

B_r = diffusivity of gaseous reactant r , cm²/sec

ρ = bulk gas density, g-mole/cm³

Equation B-18 clearly shows the dependence of the mass transfer on the heat transfer characteristics as the mass transfer coefficient, k_r , is a function of the gas film heat transfer coefficient, h_i .

Equation B-17 may be numerically integrated in the following manner. First, the heat transfer equations are solved in area increments, ΔA , for h_i and U_ℓ . The temperature of the bulk gas, t , and the interface, t_i , are calculated. A solution for the interface temperature, t_i , is obtained by equating B-2a and B-2b.

$$t_i = t - \frac{U_\ell}{h_i} (t - t_c) \quad (\text{B-19})$$

The mass transfer equations may be integrated as follows. The interface equilibrium constant, $K(t_i)$, is calculated at the surface temperature, t_i , from the thermodynamic analysis. Once the value of $P^{(\alpha_a + \alpha_s)} (y_a)^{\alpha_a} (y_s)^{\alpha_s}$ is greater than $K(t_i)$, the film is saturated and the mass transfer/deposition integration is begun. (Recalling the thermodynamic analysis in Appendix A, if the gas concentrations are greater than their equilibrium values then the system will react and form deposits, thus lowering the gas concentrations toward equilibrium.) The value of the interface mole fractions, y_{ai} and y_{si} are calculated by setting the right hand sides of Equations B-17a and B-17b equal. Equation B-20 follows from this.

$$\frac{1}{\alpha_a} k_a (y_a - y_{ai}) = \frac{1}{\alpha_s} k_s (y_s - y_{si}) \quad (\text{B-20})$$

With the assumption of negligible reaction time, the interface gas concentrations reach equilibrium.

$$K(t_i) = (P)^{(\alpha_a + \alpha_s)} (y_{ai})^{\alpha_a} (y_{si})^{\alpha_s} \quad (\text{B-21})$$

Equations B-20 and B-21 are solved simultaneously for y_{ai} and y_{si} .

With values of y_a and y_{ai} (or y_s and y_{si}) Equation B-17a (or B-17b) may be numerically integrated to solve for x at the end of the area increment, A . From the value of x , new values of y_a and y_s are calculated using Equation B-16. A new value of t_i is obtained from the heat transfer solution for the next area increment and the process is repeated.

It should be noted here that for the superheated vapor, all of the material removed from the gas is assumed to form on and be deposited on the heat transfer surface.

Case 2. Condensation From a Saturated Bulk Vapor

For this case, material can be removed from the vapor phase by condensation on the heat transfer surface and by the formation of an aerosol. The amount of aerosol is determined by the material balance.

$$\begin{array}{lcl} \text{aerosol} & & \text{total amount} \\ \text{formed} & = & \text{removed} \\ & & \text{from vapor} \end{array} - \begin{array}{l} \text{amount formed} \\ \text{on heat} \\ \text{transfer surface} \end{array} \quad (\text{B-22a})$$

$$F = G(y_{a,\text{inlet}} - y_a)/\alpha_a - Gx \quad (\text{B-22b})$$

$$F = G(y_{s,\text{inlet}} - y_s)/\alpha_s - Gx \quad (\text{B-22c})$$

where: F = moles of aerosol formed, g-moles/sec

$y_{a,inlet}$ = bulk gas NH_3 concentration at inlet of heat exchanger, ppm

$y_{s,inlet}$ = bulk gas SO_3 concentration at inlet of heat exchanger, ppm

The equations may be integrated numerically in the following manner. Condensation on the heat transfer surface begins when $K(t_i) < (P)^{(\alpha_a + \alpha_s)} (y_a)^{\alpha_a} (y_s)^{\alpha_s}$ as in the superheated case. The bulk vapor is checked for saturation in the same manner. If the bulk gas is not saturated, the mass transfer/deposition integration is calculated as before. If the bulk gas is saturated, Equations B-17a, B-17b, B-21, B-22b, B-22c, and B-24 are solved simultaneously for y_a , y_s , y_{ai} , y_{si} , F , and x .

It should be noted that the case described here is identical to the first case (superheated bulk gas) if saturation of the bulk gas is never reached. The driving force for mass transfer at the heat transfer surface for this case is equal to or less than for Case 1 (aerosol formation lowers the bulk gas concentrations, thus there is less of a concentration gradient to the surface). Therefore, aerosol formation is desirable in minimizing formation on heat transfer surfaces.

APPLICATION OF THEORETICAL MODEL TO EXPERIMENTAL SYSTEM

Dr. Ando and his associates made qualitative and quantitative tests on deposits of NH_3 - SO_3 - H_2O compounds using the apparatus shown in Figure B-1. Gaseous SO_3 , produced by heating sulfuric acid, was mixed with preheated air and ammonia. The gas mixture was heated to $400^\circ C$ in a silica tube placed in an electric heater. It then passed through a glass tube with an 0.95 cm ID and a length of 120 cm which was immersed in an oil bath. The bath was maintained at a desired temperature between 120 and $280^\circ C$. The glass tube consisted of 11 sections: 5 straight sections, 4 curved sections, and special entrance and exit sections. After the gas was passed through the tube for a specified time, the tube was removed from the bath. The inside of the tube

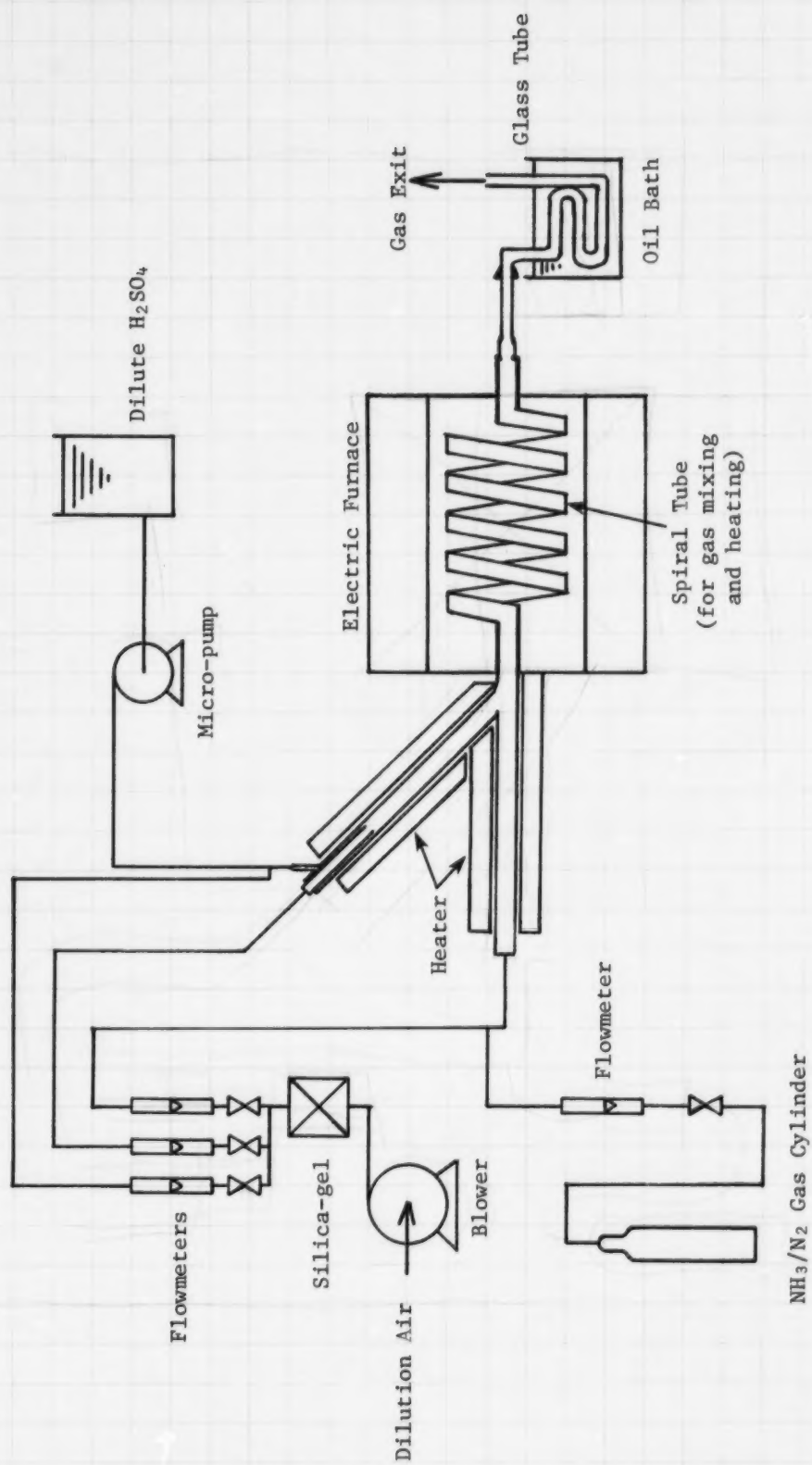


Figure B-1. Dr. Ando's Experimental Apparatus

(either each individual section or the whole tube, depending on the test) was washed with water to dissolve the deposits. The wash liquor was then analyzed chemically to determine the amount and composition of the deposits.

Tests were conducted with a gas rich in SO_3 and NH_3 (200 ppm each) because of the ease of the experiments. Tests with lower concentrations were also made and the results were similar to those with high concentrations. (All test gases contained 10 percent H_2O .) X-ray diffraction analyses showed that for the tests with 200 ppm of both NH_3 and SO_3 , the major compound formed was NH_4HSO_4 .¹⁰ There were also small amounts of a double salt, $\text{NH}_4\text{HSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$, present. This suggests that, at NH_3/SO_3 ratios close to 1.0, the kinetically favored reaction product is ammonium bisulfate. This is further confirmed by Ando's tests with inlet NH_3/SO_3 mole ratios >1 ; the deposits formed at the beginning of the tube were primarily bisulfate. Recalling the results of the thermodynamic analysis, ammonium sulfate is the thermodynamically favored product. However, thermodynamics determines the temperature range for which a chemical reaction can possibly occur, not how quickly it will occur. Therefore, for the first attempts to apply the theoretical model for the formation of ammonium sulfate compounds to experimental data, ammonium bisulfate is assumed to be the reaction product.

The theoretical model is applied to those tests of Dr. Ando in which the amount of reaction product formed was measured for each section of tube. The values for the parameters (inputs to the theoretical model) describing those tests are shown in Table B-2. In all the tests shown in Table B-2, the NH_3/SO_3 ratio was 1.0. The ability of the theoretical model to predict the location and amount of deposits in Dr. Ando's tests is central to this study.

TABLE B-2. PARAMETERS FOR THEORETICAL MODEL

Test Number	Oil Bath Temperature (°C)	Gas Velocity* (Ncm/sec)	Gas Inlet T (°C)	Gas Outlet T (°C)
1	160	100	208	161
2	160	600	338	169
3	160	1000	357	174
4	120	600	338	125

*The gas velocity units of Ncm/sec represent the volumetric flow of gas at 0°C (Ncm³/sec) through a cross-sectional area (cm²).

To characterize the phenomena of Dr. Ando's experiments, the first requisite is the determination of the combined tube wall and oil (bath) film heat transfer coefficient, α . Table B-2 shows that Dr. Ando conducted tests at three different gas velocities. Using Equation B-7, the Reynolds number is calculated for each of these velocities. (The bulk gas viscosity is calculated at an average gas temperature which is equal to the sum of the bath temperature and the log mean ΔT .) The overall average heat transfer coefficient, U_a , is calculated by Equation B-4b. The results of these calculations are shown in the table below.

TABLE B-3. WILSON PLOT DATA AT 60 cm

Test No.	V_N (Ncm/sec)	T_{gas} (°C)	Reynolds No. (Re)	$Re^{0.8}$	$1/(Re)^{0.8}$	$U_A \left(\frac{\text{cal}}{\text{cm}^2 \text{sec } ^\circ\text{C}} \right)$	$1/U_A$
1	100	208-161	471	138	7.27×10^{-3}	4.99×10^{-4}	2000
2	600	338-190	2540	530	1.90×10^{-3}	1.40×10^{-3}	711
3	1000	357-207	4110	778	1.29×10^{-3}	1.89×10^{-3}	528

The data was taken halfway through the exchanger, at 60 cm, because the 100 Ncm/sec test gas had reached its final temperature at that point. The gas temperature was approximately equal to the bath temperature at that point, so basically, no heat was transferred in the last 60 cm of the tube in that test.

A Wilson plot of $1/U_a$ versus $1/(\text{Re})^{0.8}$ is prepared using Equation B-8. This plot is shown in Figure B-2 on the following page. The data points fall very nearly on a straight line. The line is drawn through the two bottom points because they represent tests in which the gas flow pattern was transitional or turbulent ($\text{Re} > 2100$) in its character. The top point represents a laminar flow situation, for which this heat transfer correlation is not quite as accurate as for turbulent flow. The predicted value of α ($7 \times 10^{-3} \text{ cal/cm}^2 \cdot \text{sec} \cdot ^\circ\text{C}$) seems reasonable since it is on the order of magnitude of the heat transfer coefficient of just the glass tube ($12 \times 10^{-3} \text{ cal/cm}^2 \cdot \text{sec} \cdot ^\circ\text{C}$).¹¹ Recalling Equation B-7, α must then be less than $12 \times 10^{-3} \text{ cal/cm}^2 \cdot \text{sec} \cdot ^\circ\text{C}$.

Next, the gas film heat transfer coefficient correlation must be checked (corrected, if necessary) for its applicability to Ando's apparatus (which contained several curved sections). Using the value of α determined by the Wilson plot, the constant for the gas film heat transfer coefficient in Equation B-10 ($\beta = 0.023$) was varied until the predicted outlet gas temperature was within 1°C of Ando's measured outlet temperature. The results of these iterational calculations for three gas velocities are shown in Table B-4. For these tests, β is not constant although all the values are quite close to Colburn's value of .023.

Table B-4. $\beta = f(\text{Re})$

Test Number	Gas Velocity (Ncm/sec)	Re	β
1	100	471	.022
2	600	2540	.027
3	1000	4110	.029

Beta, as a function of the Reynolds number, is determined by the log-log plot of the data shown in Figure B-3.

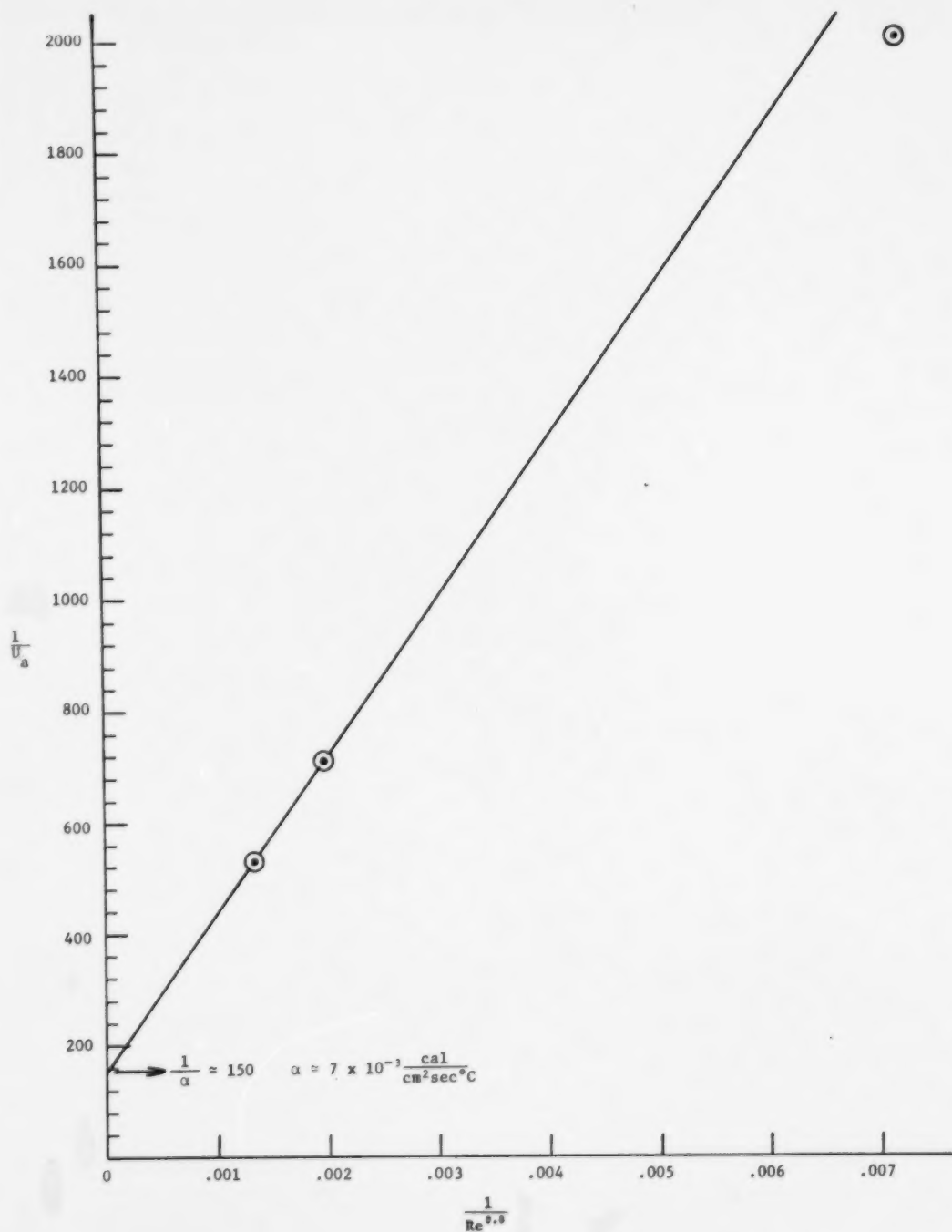


Figure B-2. Wilson Plot (at 60 cm) for Dr. Ando's tests.

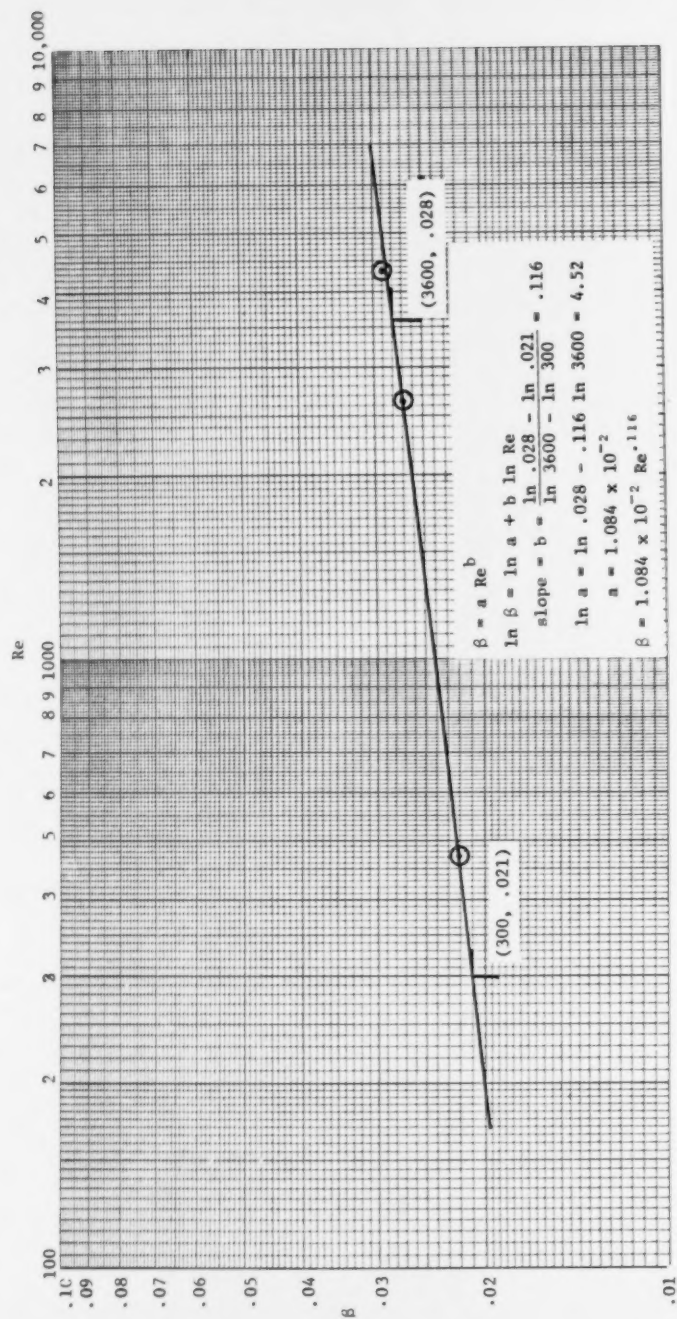


Figure B-3. Constant in gas film heat transfer coefficient correlation as a function of Reynolds number.

The gas temperature profiles predicted by the theoretically determined α and h_i agree quite well with the thermocouple measurements made during the course of the laboratory experiments.

Now that the thermodynamics (Appendix A) and the heat transfer characteristics of the system are known, the mass transfer/deposition model of the system can be applied.

RESULTS AND DISCUSSION

For each test, the heat exchanger tube is iterated over 60 increments, 2 cm in length. Knowing the bulk gas temperature and, hence, the tube wall temperature, the stagnant film layer is checked for saturation using the equilibrium expression derived from the thermodynamic analysis.

$$K = 4.60 \times 10^{-12} \exp \left[27,280 \left(\frac{1}{423} - \frac{1}{T} \right) \right] \quad (\text{B-23})$$

If the partial pressure product of the gaseous reactants is greater than the equilibrium constant (K value), then the mass transfer iteration is begun. This involves the solution of the following equations:

Material Balance

$$F = G(y_{a,\text{inlet}} - y_a) - Gx \quad (\text{B-22b})$$

$$F = G(y_{s,\text{inlet}} - y_s) - Gx \quad (\text{B-22c})$$

Mass Transfer

$$Gdx = k_a P(y_a - y_{ai}) dA \quad (\text{B-17a})$$

$$Gdx = k_s P(y_s - y_{si}) dA \quad (\text{B-17b})$$

Equilibrium

$$K(t) = P^2 y_a y_s \quad (B-24)$$

$$K(t_i) = P^2 y_{ai} y_{si} \quad (B-21)$$

where: $K(t)$ = equilibrium constant at bulk gas temperature, t , (atm^2)
 $K(t_i)$ = equilibrium constant at interface (film) temperature,
 t_i , (atm^2)

This system requires the simultaneous solution of six equations (not all linear) with six unknowns (y_a , y_{ai} , y_s , y_{si} , F and x). If the bulk gas is superheated, $F = 0$ and the system is simplified.

The results of these calculations for tests 1, 2, and 3 are shown in Figures B-4, B-5, and B-6. The figures are plots of the fractional amount of NH_3 and H_2SO_4 converted to NH_4HSO_4 in each 10-cm zone of the heat exchanger tube. The solid line in each figure is a smooth curve drawn through the data points from Dr. Ando's experimental results. The dashed lines represent the theoretical predictions from the model presented here. The lower of the two dashed lines represents only the amount of NH_4HSO_4 that actually forms at the heat transfer surface (interface) in each zone. The upper dashed line represents the sum of the condensate and aerosol that form in each zone. The exact future of an aerosol once it forms (if it deposits on the surface and, if so, where it deposits) is uncertain. This will be discussed later.

Looking at Figures B-4, B-5, and B-6 (all tests at the same oil bath temperature), an interesting trend in the condensate and aerosol curves is present. First, the peak in the aerosol curve occurs later in the tube with each test. The reason for this is that as the gas velocity increases, the gas travels further down the tube, in the same period of time, before it is cooled below the saturation temperature and aerosol formation begins. This is quite evident as the gas in Test 1 (100 Ncm/sec), shown in Figure B-4, reaches its bulk saturation temperature very near the tube entrance. The gas in Test 2 (600 Ncm/sec) doesn't reach its bulk saturation temperature

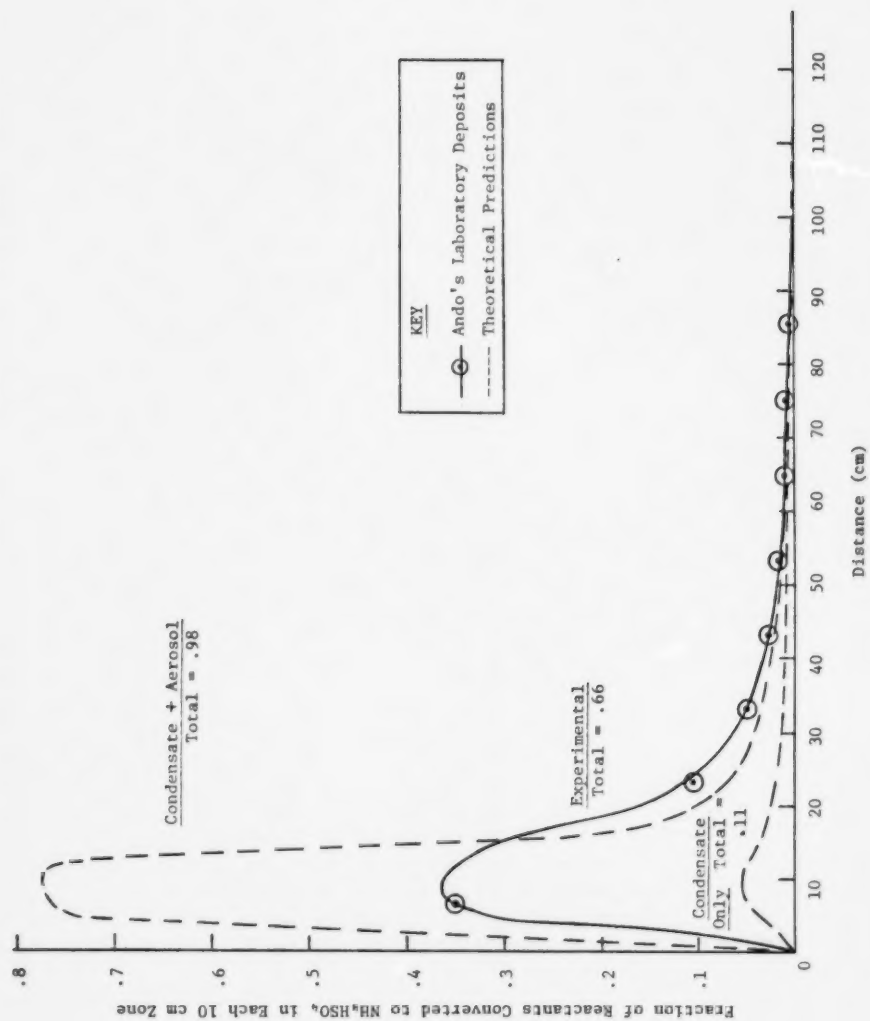


Figure B-4. Test 1: Predicted and actual NH_4HSO_4 formation for 100 Ncm/sec gas with 200 ppm each NH_3 and SO_3 , 160°C oil bath.

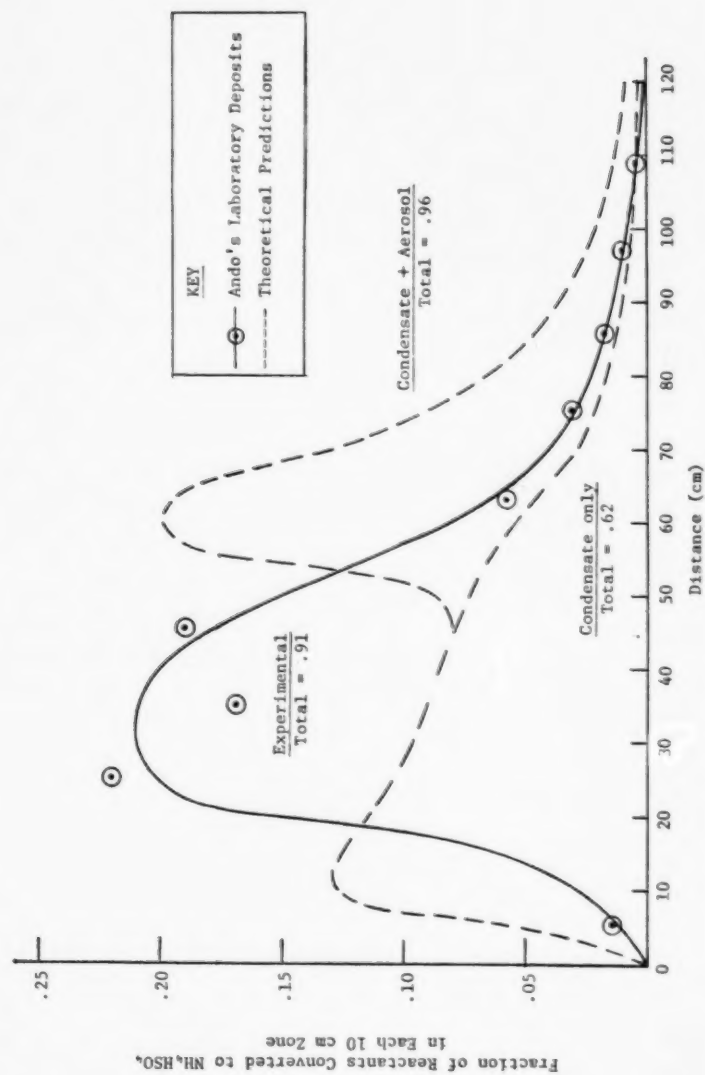


Figure B-5. Test 2: Predicted and actual NH_4HSO_4 formation for 600 Ncm/sec gas with 200 ppm each NH_3 and SO_3 , 160°C oil bath.

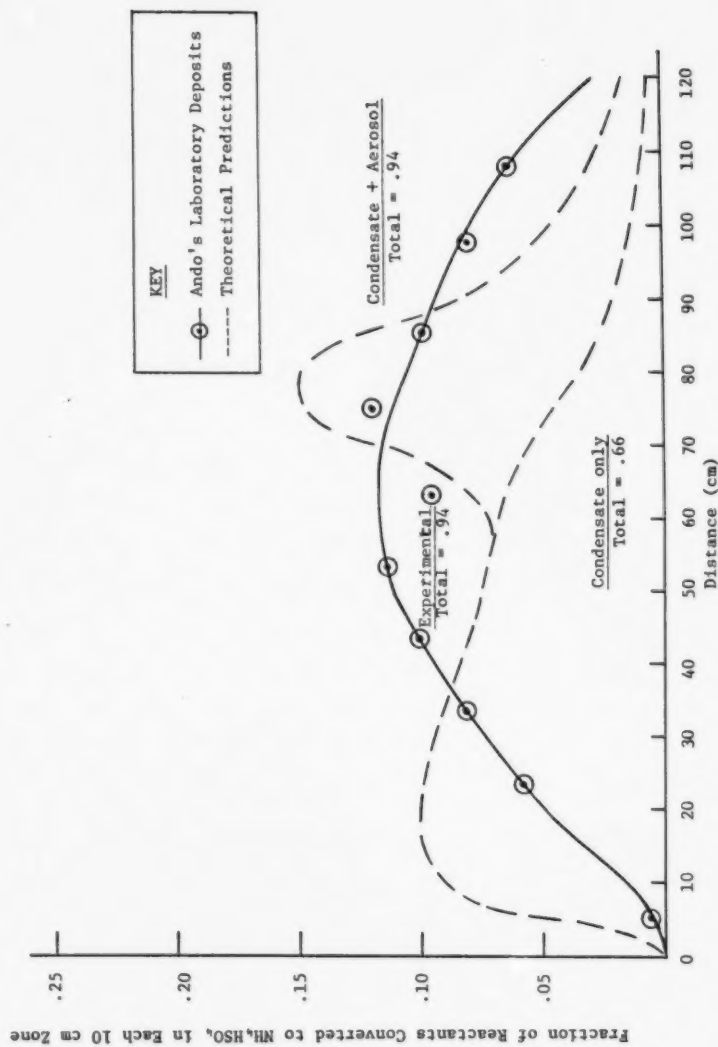


Figure B-6. Test 3: Predicted and actual NH_4HSO_4 formation for 1000 Ncm/sec gas with 200 ppm each NH_3 and SO_3 , 160°C oil bath.

until zone 5 or 6 (50 or 60 cm) while aerosol formation doesn't begin in Test 3 (1000 Ncm/sec) until the gas reaches zone 7 or 8 (70 or 80 cm).

Another trend in Figures B-4, B-5, and B-6 is that the peak in the aerosol curve is not as great with each test. Because of the delay of aerosol formation with increasing velocity, more product has a chance to form at the heat transfer surface, since the surface is cooler than the bulk gas. This is evident in the increasing amount of condensate forming at the surface and a corresponding decrease in aerosol formation, with the tests' increasing velocity. These competing mechanisms for NH_4HSO_4 formation are summarized in Table B-5.

TABLE B-5. AEROSOL CONTRIBUTION

	Test 1	Test 2	Test 3
Gas Velocity (Ncm/sec)	100	600	1000
Reynolds Number	471	2540	4110
Flow Description	laminar	transitional	turbulent
Condensate + Aerosol (%)	98	96	94
Condensate Only (%)	<u>11</u>	<u>62</u>	<u>66</u>
Aerosol Contribution (%)	87	34	28

In addition to the fact that more condensate will form at increasing gas velocities, it also appears that, at higher velocities, a larger fraction of the aerosol which forms will deposit. Table B-6 quantifies the amount of the predicted aerosol that would have to deposit to give the resultant deposit fraction that Dr. Ando measured in the laboratory. As shown, the fraction of aerosol which must deposit increases with increasing Reynolds number. In general, this trend agrees with results of previous work on aerosol deposition in tubes. Under laminar flow conditions, aerosol particles are deposited on the inner wall of a tube by diffusion of submicron size particles and by gravitational settling of micron size particles. For turbulent flow, the deposition is due to eddy (aggregate as opposed to molecular) diffusion.¹² Aerosol particles deposit when they impinge on and adhere to the wall. As

the Reynolds number increases, the random movement of the aerosol particles is significantly enhanced and the probability of the aerosol particles impinging on the wall is also increased.

TABLE B-6. AEROSOL DEPOSITION

	Test 1	Test 2	Test 3
Reynolds Number	471	2540	4110
Laboratory Deposit (%)	66	91	94
Predicted Condensate Only (%)	<u>-11</u>	<u>-62</u>	<u>-66</u>
Difference (%)	55	29	28
Predicted Aerosol Formation (%)	87	34	28
% of Predicted Aerosol which must deposit to equal difference	63	85	100

Lin¹³ estimates that as the Reynolds number approaches 10,000, nearly all the aerosol should deposit in the tube. For a laminar flow case, his estimate is about 60 percent. This agrees with the results presented in Table B-5. Verification can only be obtained through further laboratory or pilot plant studies. There are a number of other factors that must be considered including particle size, particle density, particle settling velocity, pipe or plate surface roughness, equipment geometry, etc.

Figure B-7 shows the results of Test 4 which has a gas velocity of 600 Ncm/sec and an oil bath temperature of 120°C. Comparing this to Test 2 (Figure B-5), the same gas velocity in a 160°C bath, the shapes of the 2 curves are quite similar. Test 4 shows an earlier and larger peak due to aerosol formation, which is to be expected. The bulk gas is cooled to its saturation temperature earlier in the tube, resulting in more aerosol formation.

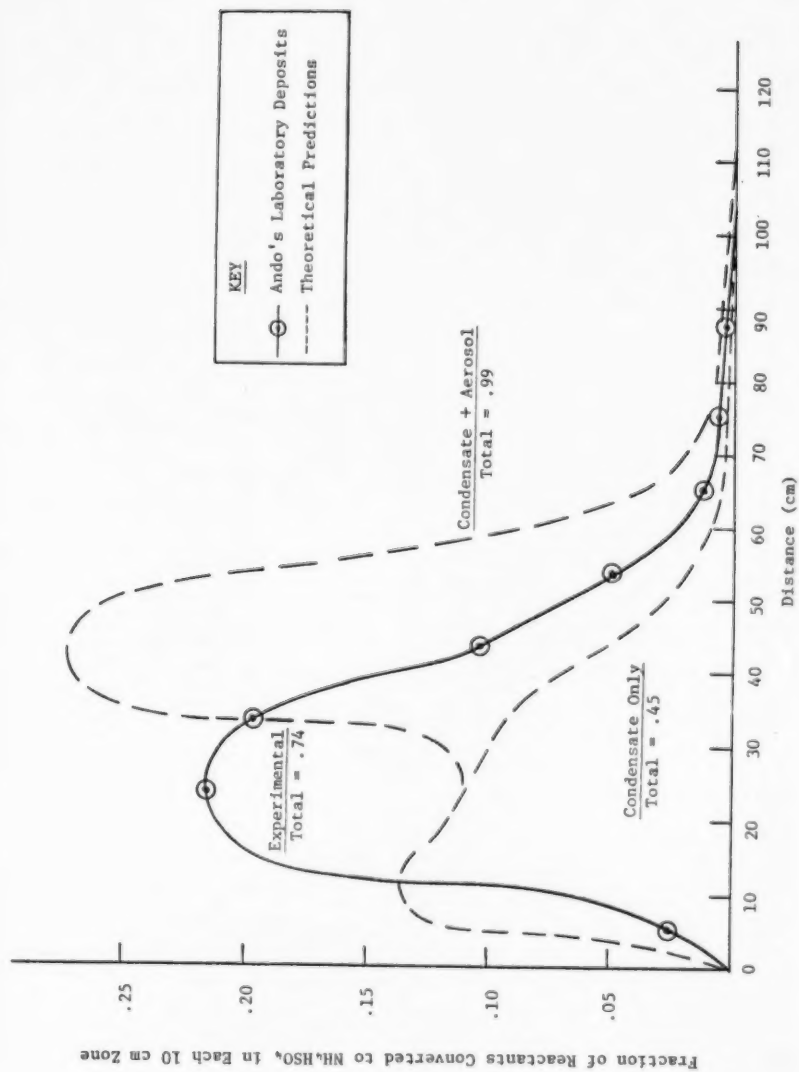


Figure B-7. Test 4: Predicted and actual NH_4HSO_4 formation for 600 Ncm/sec gas with 200 ppm each NH_3 and SO_3 , 120°C oil bath.

The results of the model's predictions presented in Figures B-4 through B-7 are similar to those obtained in the laboratory experiments. (Tests 2 and 3 show a second peak in Ando's data points that correspond to the predicted aerosol formation. The experimental points could be due to the onset of aerosol formation or to unique apparatus geometry.) This indicates that the application of basic chemical engineering principles can approximate the chemical and physical phenomena of the $\text{NH}_3/\text{H}_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ system. However, the work presented here is an initial attempt at describing one experimental situation. The problem of applying this model to air preheater systems is not trivial. With detailed process data and pilot studies of the NH_4HSO_4 /air preheater system (particularly in the area of aerosol formation/deposition), the phenomena can be described precisely.

In summary, the modeling results have several implications in terms of an air preheater system. For Ando's laboratory tests the assumptions made in developing the model appear to be valid. At an initial NH_3/SO_3 mole ratio of 1.0, the principal reaction product appears to be NH_4HSO_4 and the reaction which forms this product is very rapid. The fact that NH_4HSO_4 is the principal product formed is in apparent conflict with the thermodynamic predictions which indicate that $(\text{NH}_4)_2\text{SO}_4$ should be the only compound which forms, regardless of the initial NH_3/SO_3 stoichiometric ratio.

Apparently, the reaction which forms $(\text{NH}_4)_2\text{SO}_4$ directly from gas phase reactants is slow relative to both the rate at which the gas is cooled from the sulfate to the bisulfate formation temperature and the rate of the reaction which produces NH_4HSO_4 . As a consequence, the gas is cooled below both the $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 formation temperatures before appreciable quantities of $(\text{NH}_4)_2\text{SO}_4$ can form. At this point, the formation of NH_4HSO_4 predominates due to its more rapid reaction rate. This is not to imply that no $(\text{NH}_4)_2\text{SO}_4$ will form in a preheater. On the contrary, significant quantities of $(\text{NH}_4)_2\text{SO}_4$ will form in the presence of excess NH_3 .

It appears that NH_4HSO_4 formed in an air preheater system will react with excess NH_3 to form $(\text{NH}_4)_2\text{SO}_4$ since there is a thermodynamic driving force for this reaction. As the quantity of excess NH_3 increases, the fraction of $(\text{NH}_4)_2\text{SO}_4$ formed will also increase. However, with available data, it is not possible to predict the minimum NH_3/SO_3 ratio at which $(\text{NH}_4)_2\text{SO}_4$ is the only product.

The primary factors controlling NH_4HSO_4 and subsequent $(\text{NH}_4)_2\text{SO}_4$ formation are the concentrations of the gaseous reactants and the system temperatures. For given reactant concentrations, there is a specific temperature above which NH_4HSO_4 will not form. The question of NH_4HSO_4 deposition is more complex. The relative rates of heat and mass transfer must be considered to predict the amount of deposits. If the gas is cooled rapidly, significant amounts of NH_4HSO_4 aerosol will form in the bulk gas. Depending on system parameters (gas velocity, gas passing area, particle characteristics, etc.), some of the aerosol formed should pass through the preheater. To make accurate estimates of the amount of ammonium sulfates which form and deposit in an air preheater, detailed analysis of air preheater design and operation along with development of more fundamental data on $\text{NH}_3\text{-SO}_3$ reactions is needed.

APPENDIX B
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APPENDIX C

ESTIMATED ENERGY CONSUMPTION, MATERIAL FLOWS, AND CAPITAL AND OPERATING COSTS FOR POTENTIAL SOLUTIONS TO THE $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$ DEPOSITION PROBLEM

This appendix documents the calculations which were performed to estimate the energy consumption and costs associated with the proposed solutions presented in Section 6 of the report. All assumptions made in performing the calculations are also presented in this appendix.

The basis for the cost analysis presented in this appendix was drawn from three sources. The air preheater and soot blower capital costs were based on a quote/specifications supplied by C-E Air Preheater Division of Combustion Engineering, Inc.¹ The specifications also identified the energy consumption for each soot blower. The installed costs for the air preheater including indirect costs were estimated using the cost factors for field erected boilers from K. M. Guthrie's "Process Plant Estimating Evaluation and Control".² The third source used in developing the calculations presented in this appendix was the "Preliminary Economic Analysis of NO_x Flue Gas Treatment Processes" prepared by TVA.³ The information from TVA's report was used as a basis for flue gas flows and temperatures. Also, fan costs and costs for catalyst and reactors were taken from TVA's report.

The calculations presented in this appendix are included with all the assumptions used in developing them. They are presented here to provide documentation and a basis for more detailed evaluation of the proposed solutions. Because of the nature of the solutions presented in Section 6, the cost estimates are rough. To obtain more accurate estimates, detailed equipment designs and costing are required.

ESTIMATED ENERGY CONSUMPTION FOR AIR PREHEATER SOOT BLOWING BASE CASE

Base Case Soot Blowing

- 1 soot blower per preheater
- 2 preheaters
- 3 soot blowing cycles per day

Steam Consumption Per Cycle

- 255 lb steam per minute
- 11 minutes per cycle
- 200 psig steam at 1354 Btu/lb

For the base case:

$$(2 \text{ preheaters}) \left(\frac{1 \text{ soot blower}}{\text{preheater}} \right) \left(\frac{255 \text{ lb steam}}{\text{soot blower min}} \right) \left(\frac{1354 \text{ Btu}}{\text{lb steam}} \right) \\ \left(\frac{11 \text{ min}}{\text{cycle}} \right) \left(\frac{3 \text{ cycles}}{\text{day}} \right) \left(\frac{1 \text{ day}}{24 \text{ hrs}} \right) = 0.95 \times 10^6 \text{ Btu/hr}$$

ESTIMATED CAPITAL COST FOR BASE CASE AIR PREHEATER

Base Equipment Cost = 2,125,000

Material Factor = (22.4%)(.065) = 1.5%

Labor Factor = (19.5%)(.82) = 16.0%

Indirect Factor = (1.28)(.82) = 1.05

Installed Cost for Base Case

$$(\$2,125,000) \left[1 + \left(\frac{1.5\% + 16.0\%}{100} \right) (1.05) \right] = \$2,621,700$$

ESTIMATED ENERGY CONSUMPTION FOR AIR PREHEATER DESIGN OPTIONS

Modified Soot Blowers

6 cycles/day

6 soot blowers per preheater

250 psig steam at 1373 Btu/lb

$$(2 \text{ preheaters}) \left(\frac{6 \text{ soot blowers}}{\text{preheater}} \right) \left(\frac{255 \text{ lb steam}}{\text{soot blower min}} \right) \left(\frac{1373 \text{ Btu}}{\text{lb steam}} \right)$$

$$\left(\frac{11 \text{ min}}{\text{cycle}} \right) \left(\frac{6 \text{ cycles}}{\text{day}} \right) \left(\frac{1 \text{ day}}{24 \text{ hrs}} \right) = 11.5 \times 10^6 \text{ Btu/hr}$$

ESTIMATED CAPITAL COSTS FOR AIR PREHEATER DESIGN OPTIONS

Base Equipment Cost = \$2,125,000

Cost for Each Soot Blower = \$12,840

Cost for 304SS in intermediate temperature zone of both preheaters = \$1,115,000

Total Equipment Costs for Options

$$\$2,125,000 + (10)(\$12,840) + \$1,115,000 = \$3,368,400$$

Assume same installation cost factor as base case

Total Installed Costs

$$(\$3,368,400)(1 + 0.015 + 0.16)(1.05) = \$4,155,764$$

ESTIMATED INCREMENTAL CAPITAL AND ANNUALIZED COSTS FOR AIR PREHEATER
DESIGN OPTIONS

Incremental Capital Costs

$$\$4,155,764 - \$2,621,720 = \$1,534,044$$

Incremental Annualized Costs

Annualized costs result from increased capital costs, from increased fuel consumption, and from increased wastewater flows. The capital recovery factor used in this analysis is 14.6 percent and was derived from TVA's economic analysis. The costs for waste treatment are incremental costs and based on alkali precipitation.

Incremental Annualized Capital Costs

$$(\$1,534,044)(.146) = \$223,970/\text{yr}$$

First Year Incremental Annualized Fuel Costs

$$\begin{aligned} & (11.5 \times 10^6 \text{ Btu/hr} - 0.95 \times 10^6 \text{ Btu/hr}) (7000 \text{ hrs/yr}) \left(\frac{1}{.88} \text{ thermal efficiency}\right) \\ & \times \frac{\$2.5}{10^6 \text{ Btu}} = \$209,801/\text{yr} \end{aligned}$$

Incremental Annualized Water Treatment Costs

Assume water washing is required 4 times per year and duration of washing is 8 hours. For a size 31 preheater, 91 inches deep, wash water rate = 2050 gpm.

$$\text{Annual Water Consumption} = \left(\frac{2050 \text{ gal}}{\text{preheater} \cdot \text{min}} \right) (2 \text{ preheaters}) \left(\frac{60 \text{ min}}{\text{hr}} \right) \left(\frac{8 \text{ hrs}}{\text{wash cycle}} \right) \left(\frac{3 \text{ incremental cycles}}{\text{year}} \right) = 5.9 \times 10^6 \text{ gal/yr}$$

For lime precipitation estimated treatment cost = \$3/1000 gal

Annual Costs = $5.9 \times 10^6 \text{ gal/yr} \times \$3.0/1000 \text{ gal} = \$17,700/\text{yr}$

Total Incremental Annualized Costs

Capital Costs + Fuel Costs + Water Treatment Costs

$\$223,970/\text{yr} + \$209,801/\text{yr} + \$17,700/\text{yr} = \$451,471/\text{yr}$

ESTIMATED ENERGY CONSUMPTION FOR AIR PREHEATER HEAT CLEANING

Assume heat cleaning requires 10% of design flow for 30 min.

Full load flow/preheater = 41,000 lb/min.

At 10 percent flow = $41,000 (1\text{b/min})(0.1) = 4,100 \text{ lb/min.}$

Heat capacity of flue gas $\approx 0.25 \text{ Btu/lb } ^\circ\text{F}$

ΔT during heat cleaning cycle is $350^\circ\text{C} - 150^\circ\text{C} = 200^\circ\text{C} = 360^\circ\text{F}$

Duration of heat cleaning cycle is 30 min. Then heat loss can be estimated.

$$\left(4,100 \frac{\text{lb}}{\text{min}} \right) \left(\frac{30 \text{ min}}{\text{cycle}} \right) \left(\frac{1 \text{ cycle}}{\text{day}} \right) \left(\frac{1 \text{ day}}{24 \text{ hrs}} \right) \left(360^\circ\text{F} \right) \left(\frac{0.25 \text{ Btu}}{\text{lb}^\circ\text{F}} \right) \left(2 \text{ preheaters} \right) =$$

heat loss (hourly average) = $0.92 \times 10^6 \text{ Btu/hr}$

ESTIMATED CAPITAL COSTS FOR AIR PREHEATER HEAT CLEANING

Costs for 304 SS in the intermediate/low temperature zone of the preheater = \$1,115,000.

Costs for air dampers for isolation/flow control assumed to be \$25,000 each. 8 dampers required = $(8)(25,000) = \$200,000$

Cost for control system assumed to be 50 percent of damper costs = \$100,000.

Total Capital Costs =

$$\$2,125,000 + \$1,115,000 + 200,000 + 100,000 = \$3,540,000$$

Assume cost factors do not change since preheater size remains constant. Then total installed costs for preheater can be estimated:

$$(\$3,540,000)(1.175)(1.05) = \$4,367,700$$

ESTIMATED INCREMENTAL CAPITAL AND FIRST YEAR ANNUALIZED COSTS FOR AIR PREHEATER HEAT CLEANING

Incremental Capital Costs

$$\$4,367,700 - \$2,621,700 = \$1,746,000$$

Incremental Annualized Costs

$$\text{Capital Component} = (\$1,746,000)(.146) = \$254,900/\text{year}$$

Fuel Cost Component =

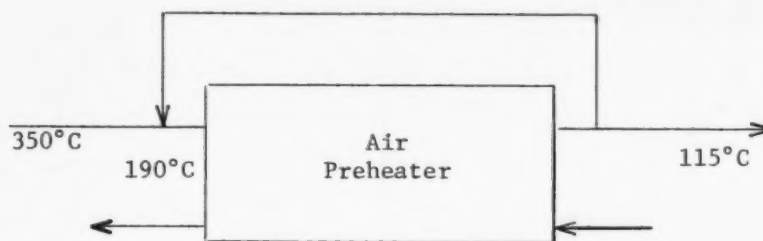
$$\left(0.92 \times 10^6 \frac{\text{Btu}}{\text{hr}} \right) \times \frac{7000 \text{ hrs}}{\text{yr}} \times \frac{\$2.5}{10^6 \text{ Btu}} = \$16,100/\text{yr}$$

Total Incremental Annualized Costs

Capital Charges + Fuel Costs = Total Annualized Costs

$$\frac{\$254,900}{\text{year}} + \frac{\$16,100}{\text{year}} = \frac{\$271,000}{\text{year}}$$

ESTIMATED ENERGY CONSUMPTION FOR FLUE GAS RECIRCULATION



Material and Energy Balance for Single Air Preheater

Recirculation Rate = x

$$(82,000)(350) + (115)(x) = 190(82,000 + x)$$

$$x = 175,000 \text{ lb/min}$$

Energy Savings for Lower Outlet Temperature

$$(150-115^\circ\text{C}) \left(\frac{1.8^\circ\text{F}}{^\circ\text{C}} \right) \left(0.25 \frac{\text{Btu}}{\text{lb}^\circ\text{F}} \right) \left(\frac{82000 \text{ lb}}{\text{min}} \right) \left(\frac{60 \text{ min}}{\text{hr}} \right) = 77.5 \times 10^6 \text{ Btu/hr}$$

Energy Penalty for Flue Gas Recirculation

Assume ΔP for recirculated gas = 10 in H_2O

Gas Flowrate =

$$175,000 \frac{\text{lb}}{\text{min}} \times \frac{1 \text{ lb mole}}{29 \text{ lb}} \times \frac{379 \text{ scf}}{\text{lb mole}} \times \frac{700 \text{ acf}}{520 \text{ scf}} = 3.08 \times 10^6 \text{ acfm}$$

Pressure Drop

$$10 \text{ in H}_2\text{O} \times \frac{1 \text{ ft}}{12 \text{ in}} \times \frac{1 \text{ atm}}{33.9 \text{ ft}} \times \frac{14.7 \text{ psi}}{\text{atm}} = 0.36 \text{ psi}$$

Energy Consumption

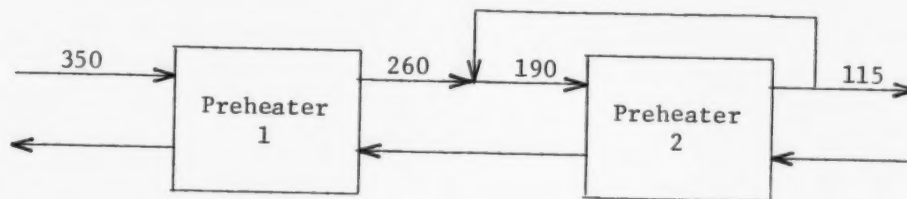
$$\text{Shaft hp} = \frac{144 Q \Delta P}{(0.7)(33,000)} = \frac{(144)(3.08 \times 10^6)(.36)}{(33,000)(0.7)} = 6.91 \times 10^3 \text{ hp}$$

$$\frac{6.91 \times 10^6 \text{ hp}}{.379} \times 42.42 \frac{\text{Btu}}{\text{min}} \times \frac{60 \text{ min}}{\text{hr}} = 46.4 \times 10^6 \text{ Btu/hr}$$

Net Savings

$$77.5 \times 10^6 \frac{\text{Btu}}{\text{hr}} - 46.4 \times 10^6 \frac{\text{Btu}}{\text{hr}} = 31.9 \times 10^6 \text{ Btu/hr}$$

Material and Energy Balance for Split Air Preheater



$$\text{Recirculation Rate} = x$$

$$(82,000)(260) + (x)(115) = (82,000 + x)(190)$$

$$x = 76,500$$

Energy Savings

$$82,000 \frac{\text{lb}}{\text{min}} (150-115^\circ\text{C}) \frac{1.8^\circ\text{C}}{^\circ\text{F}} \frac{.25 \text{ Btu}}{\text{lb } ^\circ\text{F}} \frac{60 \text{ min}}{\text{hr}} = 77.5 \times 10^6 \text{ Btu/hr}$$

Energy Loss

Assume ΔP for Recirculation = 7 in H_2O = 0.25 psi

$$Q = \left(76,500 \frac{\text{lb}}{\text{min}} \right) \left(\frac{1 \text{ lb mol}}{29 \text{ lb}} \right) \left(\frac{379 \text{ scf}}{1 \text{ lb mole}} \right) \left(\frac{700 \text{ acf}}{520 \text{ scf}} \right) = 1.35 \times 10^6 \text{ acfm}$$

$$\text{Shaft hp} = \frac{(144)(Q)(\Delta P)}{(0.7)(33,000)} = \frac{(144)(1.35 \times 10^6)(0.25)}{(33,000)(0.7)} = 2.13 \times 10^3 \text{ hp}$$

$$\text{Fan Energy} = \left(\frac{2.13 \times 10 \text{ hp}}{.379} \right) \left(\frac{42.42 \text{ Btu}}{\text{hp} \cdot \text{min}} \right) \left(\frac{60 \text{ min}}{\text{hr}} \right) = 14.3 \times 10^6 \text{ Btu/hr}$$

Net Savings

$$77.5 \times 10^6 \text{ Btu/hr} - 14.3 \times 10^6 \text{ Btu/hr} = 63.2 \times 10^6 \text{ Btu/hr}$$

ESTIMATED CAPITAL COSTS FOR FLUE GAS RECIRCULATION

Single Air Preheater Design Option

$$\text{New Flue Gas Flowrate} = 175,000 + 82,000 \text{ lb/min} = 257,000 \text{ lb/min}$$

$$\text{Air Flowrate} = 80,000 \text{ lb/min}$$

Relative total flowrates for base case and single preheater - flue gas recirculation

$$\frac{257,000 + 80,000}{82,000 + 80,000} = 2.08$$

Assume that the preheater size increases in direct proportion to the gas flowrate and no economy of scale is realized.

New Preheater Equipment Costs

$$\$2,125,000 \times 2.08 = \$4,420,000$$

Installed Costs

For larger preheater cost factor for installation is changed.

$$\text{Installed cost factor}^2 = 1.20$$

$$\text{Installed costs} = \$4,420,000(1.2) = \$5,304,000$$

Costs of Fans for Recirculation

For 1 blower 772,000 acfm, $\Delta P = 21$ in H_2O , 4000 hp, 316 SS total capital cost³ = \$1,430,000

$$\text{Recirculation Rate} = 3.08 \times 10^6 \text{ acfm}$$

Again, assume no economy of scale.

$$\text{Fan costs are: } \frac{3.08 \times 10^6}{772,000} = 3.99$$

$$3.99 \times \$1,430,000 = \$5,705,000$$

Cost for Reaction Chamber for Single Preheater Recirculation

$$1979 \text{ insulated duct cost (installed)} = \$28.50/\text{ft}^2$$

Assume: 2 reaction chambers (1 per preheater)

Duct w/square crossection

Residence time = 2.0 seconds

Gas velocity = 40 ft/sec

Gas molecuolor wt = 29 lb/lb mole

For the single preheater

Gas temperature = $190^{\circ}\text{C} = 834^{\circ}\text{R}$

Gas flowrate = 257,000 lb/min (total)

= 128,500 lb/min/reaction chamber

Gas flowrate (acfm) =

$$128,500 \frac{\text{lb}}{\text{min}} \times \frac{1 \text{ lb mole}}{29 \text{ lb}} \times \frac{379 \text{ scf}}{1 \text{ lb mole}} \times \frac{834 \text{ acf}}{520 \text{ scf}} = 2,700,000 \text{ acfm}$$

Duct crossection =

$$2,700,000 \frac{\text{ft}^3}{\text{min}} \times \frac{1 \text{ min}}{60 \text{ sec}} \times \frac{\text{sec}}{40 \text{ ft}} = 1125 \text{ ft}^2$$

$$\text{Duct area/ft of duct} = \sqrt{1125 \times 4} = 134 \text{ ft}^2/\text{ft}$$

$$\text{Total duct area} = \frac{40 \text{ ft}}{\text{sec}} \times 2 \text{ sec} \times \frac{134 \text{ ft}^2}{\text{ft}} = 10720 \text{ ft}^2$$

Total installed cost for reaction chamber = \$305,500

Total cost for system = $2 \times \$305,500 = \$611,000$

Costs for Recirculation Duct Single Preheater

Assume: 2 ducts required (1 per preheater)

Duct length = 1.5 length of Rxn chamber = 120 ft

Duct w/square crossection

Gas velocity = 40 ft/sec

Gas molecular wt = 29

For the single preheater design

Recirculation gas temperature = $115^{\circ}\text{C} = 699^{\circ}\text{R}$

Recirculation gas flowrate = 175,000 lb/min

= 87,500 lb/min/preheater

Gas flowrate (acfm) =

$$87,500 \frac{\text{lb}}{\text{min}} \times \frac{1 \text{ lb mole}}{29 \text{ lbs}} \times \frac{379 \text{ scf}}{1 \text{ lb mole}} \times \frac{699 \text{ acf}}{520 \text{ scf}} = 1,540,000 \text{ acfm}$$

Duct crossection =

$$1,540,000 \frac{\text{ft}^3}{\text{min}} \times \frac{1 \text{ min}}{60 \text{ sec}} \times \frac{1 \text{ sec}}{40 \text{ ft}} = 642 \text{ ft}^2$$

Duct area/ft of duct = $\sqrt{642} \times 4 = 101 \text{ ft}^2/\text{ft}$

Total duct area = $120 \text{ ft} \times 101 \frac{\text{ft}^2}{\text{ft}} = 12120 \text{ ft}^2$

Total installed cost for recirculation ducts =

$$12120 \frac{\text{ft}^2}{\text{duct}} \times 2 \text{ recirculation ducts} \times \frac{\$28.50}{\text{ft}^2} = \$690,800$$

Split Air Preheater Design

Relative Size of Air Preheaters 1 and 2

For base case air preheater, cold end metal temperature is 210°C [the $(\text{NH}_4)_2\text{SO}_4$ formation temperature] at approximately (20/55) through the preheater.

Relative Size = $20/55 = 0.36$

Assuming scale factor = 0.5

Cost = $2,125,000 (0.36)^{0.5} = \$1,275,000$

For Preheater 2, Relative size =

$[(76,500 + 82,000) + 80,000]/(82,000 + 80,000) = 1.47$

Again, assuming no economy of scale costs are =

$(1.47) (\$2,128,000) = \$3,123,800$

Installed Costs for Preheaters

	Equipment Costs	x	Cost Factor	=	Installed Costs
Preheater 1	\$1,275,000	x	1.30	=	\$1,657,500
Preheater 2	\$3,123,800	x	1.20	=	\$3,748,600
Total				=	\$5,406,100

Fan Costs

Recirculation Rate = 1.35×10^6 acfm

$$\text{Fan Costs (installed)} = \left(\frac{1,350,000 \text{ acfm}}{772,000 \text{ acfm}} \right) \left(\frac{\$1,430,000}{\text{fan}} \right) = \$2,501,000$$

Cost for Reaction Chamber for Split Preheater Recirculation

1979 insulated duct cost (installed) = \$28.50/ft²

Assume: 2 reaction chambers

Duct w/square crossection

Residence time = 2.0 seconds

Gas velocity = 40 ft/sec

Gas molecular wt = 29 lb/lb mole

For the split preheater

Gas temperature = 190°C = 834°R

Gas flowrate = 158,500 lb/min (total)

= 79,300 lb/min/reaction chamber

Gas flowrate (acfm) =

$$79,300 \frac{\text{lb}}{\text{min}} \times \frac{1 \text{ lb mole}}{29 \text{ lb}} \times \frac{379 \text{ scf}}{1 \text{ lb mole}} \times \frac{834 \text{ acf}}{520 \text{ scf}} = 1,660,000 \text{ acfm}$$

Duct crossection =

$$1,660,000 \frac{\text{ft}^3}{\text{min}} \times \frac{1 \text{ min}}{60 \text{ sec}} \times \frac{1 \text{ sec}}{40 \text{ ft}} = 692 \text{ ft}^2$$

$$\text{Duct area/ft of duct} = \sqrt{692} \times 4 = 105 \text{ ft}^2/\text{ft}$$

$$\text{Total duct area} = \frac{40 \text{ ft}}{\text{sec}} \times 2 \text{ sec} \times 105 \frac{\text{ft}^2}{\text{ft}} = 8400 \text{ ft}^2$$

Total installed cost for reaction chamber = \$239,400

Total cost for system (2 Rxn Chambers) = 2 x \$239,400 = \$478,800

Costs for Recirculation Duct Split Preheater

Assume: 2 ducts required (1 per preheater)

Duct length = 120 ft

Duct w/square crossection

Gas velocity = 40 ft/sec

Gas molecular wt = 29

For the split preheater design

Recirculation gas temperature = 115°C = 699°R

Recirculation gas flowrate = 76,500 lb/min (total)

38,300 lb/min/preheater

Gas flowrate (acfm) =

$$38,300 \frac{\text{lb}}{\text{min}} \times \frac{1 \text{ lb mole}}{29 \text{ lbs}} \times \frac{379 \text{ scf}}{1 \text{ lb mole}} \times \frac{699 \text{ acf}}{520 \text{ scf}} = 673,000 \text{ acfm}$$

Duct crossection =

$$673,000 \frac{\text{ft}^3}{\text{min}} \times \frac{1 \text{ min}}{60 \text{ sec}} \times \frac{1 \text{ sec}}{40 \text{ ft}} = 281 \text{ ft}^2$$

$$\begin{aligned}\text{Duct area/ft of duct} &= \sqrt{281} \times 4 = 67 \text{ ft}^2/\text{ft} \\ \text{Total duct area} &= 120 \text{ ft} \times 67 \frac{\text{ft}^2}{\text{ft}} = 8040 \text{ ft}^2\end{aligned}$$

Total installed cost for recirculation ducts =

$$8040 \text{ ft}^2 \times 2 \text{ recirculation ducts} \times \frac{\$28.50}{\text{ft}^2} = \$458,300$$

FIRST YEAR ANNUALIZED COSTS FOR RECIRCULATION SINGLE PREHEATER

Energy Savings

$$\left(31.9 \times 10^6 \text{ Btu/hr}\right) \left(\frac{\$2.5}{10^6 \text{ Btu}}\right) \left(\frac{7000 \text{ hrs}}{\text{yr}}\right) = \$558,300/\text{year}$$

Annualized Capital Costs (net)

Incremental Preheater Costs	Recirculation Fan Costs	Reaction Chamber Costs	Recirculation Duct Costs	Net Cost Increase
(\$5,304,000-\$2,621,700)+\$5,706,000	+	\$611,000	+	\$690,800 = \$9,690,100

$$\text{Annual capital charges} = (\$9,690,100) (.146) = \$1,414,800$$

FIRST YEAR ANNUALIZED COSTS FOR RECIRCULATION SPLIT PREHEATER

Net Energy Savings

$$\frac{63.2 \times 10^6 \text{ Btu}}{\text{hr}} \times \frac{\$2.5}{10^6 \text{ Btu}} \times \frac{7000 \text{ hrs}}{\text{yr}} = \$1,106,000$$

First Annualized Capital Costs (net)

Incremental Preheater Costs	Recirculation Fan Costs	Reaction Chamber Costs	Recirculation Duct Costs	Net Cost Increase
(\$5,406,100-\$2,621,700)+\$2,501,000	+	\$478,800	+	\$458,300 = \$6,222,500

$$\text{Annual capital charges} = (\$6,222,500) (.146) = \$908,500$$

ESTIMATED ENERGY CONSUMPTION FOR INCREASING COLD-END METAL TEMPERATURE

The energy penalty can be estimated on a 1°C basis by assuming a constant value for the heat capacity = $0.25 \frac{\text{Btu}}{\text{lb}^\circ\text{F}}$.

$$\frac{\text{Energy Penalty}}{^\circ\text{C}} = \frac{82,000 \text{ lb}}{\text{min}} \times \frac{1.8^\circ\text{F}}{^\circ\text{C}} \times \frac{0.25 \text{ Btu}}{\text{lb}^\circ\text{F}} \times \frac{60 \text{ min}}{\text{hr}} = \frac{2.2 \times 10^6 \text{ Btu}}{^\circ\text{C} \cdot \text{hr}}$$

For prevention of NH_4HSO_4 formation, $\Delta T = 80^\circ\text{C}$

$$\text{Energy Penalty} = \frac{2.2 \times 10^6 \text{ Btu}}{^\circ\text{C} \cdot \text{hr}} \times 80^\circ\text{C} = \frac{177 \times 10^6 \text{ Btu}}{\text{hr}}$$

For prevention of $(\text{NH}_4)_2\text{SO}_4$ formation, $\Delta T = 110^\circ\text{C}$

$$\text{Energy Penalty} = \frac{2.2 \times 10^6 \text{ Btu}}{\text{hr } ^\circ\text{C}} \times 110^\circ\text{C} = \frac{244 \times 10^6 \text{ Btu}}{\text{hr}}$$

ESTIMATED INCREMENTAL ANNUALIZED COSTS FOR INCREASING COLD-END METAL TEMPERATURE

Assume no change in capital costs although size and cost of air pre-heater may be reduced.

For prevention of NH_4HSO_4 formation

$$\text{Annualized costs} = \frac{177 \times 10^6 \text{ Btu}}{\text{hr}} \times \frac{\$2.5}{10^6 \text{ Btu}} \times \frac{7000 \text{ hrs}}{\text{yr}} = \$3,097,500/\text{yr}$$

For prevention of $(\text{NH}_4)_2\text{SO}_4$ formation

$$\text{Annualized costs} = \frac{244 \times 10^6 \text{ Btu}}{\text{hr}} \times \frac{\$2.5}{10^6 \text{ Btu}} \times \frac{7000 \text{ hrs}}{\text{yr}} = \$4,270,000/\text{yr}$$

ESTIMATED ENERGY CONSUMPTION FOR SCR SYSTEM DESIGN CHANGES

The only potential changes in energy consumption from the base case are increased electricity consumption due to increased reactor pressure drop (because of the extra catalyst) and decreased steam usage for NH_3 vaporization (due to lower NH_3/NO_x). However, for this analysis it was assumed that the reactors with additional catalyst are designed with slightly larger cross-sectional areas so that the pressure drop is the same as that for the base case. Also, the NH_3/NO_x ratios do not change significantly, hence, the change in energy required for NH_3 vaporization is negligible.⁴

ESTIMATED INCREMENTAL ANNUALIZED COSTS FOR INCREASED CATALYST

To calculate the additional catalyst required for maintaining 90 percent NO_x removal while reducing the NH_3 emissions, it was assumed that the NO_x reduction reaction is first order. The rate expression for such a reaction is given by the equation⁵

$$-\ln \frac{(\text{NO}_x)_{\text{OUT}}}{(\text{NO}_x)_{\text{IN}}} = kt$$

where

$(\text{NO}_x)_{\text{OUT}}$ = outlet NO_x concentration

$(\text{NO}_x)_{\text{IN}}$ = inlet NO_x concentration

k = rate constant

t = time required for reaction

For 90 percent NO_x removal:

$$\frac{(\text{NO}_x)_{\text{OUT}}}{(\text{NO}_x)_{\text{IN}}} = 0.1$$

$$kt = -\ln 0.1$$

$$t = \frac{2.30}{k}$$

For 99 percent NO_x removal:

$$\frac{(\text{NO}_x)_{\text{OUT}}}{(\text{NO}_x)_{\text{IN}}} = 0.01$$

$$kt = -\ln 0.01$$

$$t = \frac{4.60}{k}$$

For this analysis, the relative amount of catalyst is considered to be equivalent to a relative amount of time. Physically, with gas velocity constant, doubling the length of the reactor will double the time the gas is in contact with the catalyst. Therefore, the direct relating of relative catalyst amounts to relative reaction time is appropriate. For a first order reaction, the relative amount of catalyst required for 99 percent reaction is twice that required for 90 percent reaction. This relationship is shown graphically in Figure C-1.

Example Calculation

If, for example, 10 percent additional catalyst is used, the relative amount of catalyst (compared to the base case) is 1.1. Figure C-1 shows

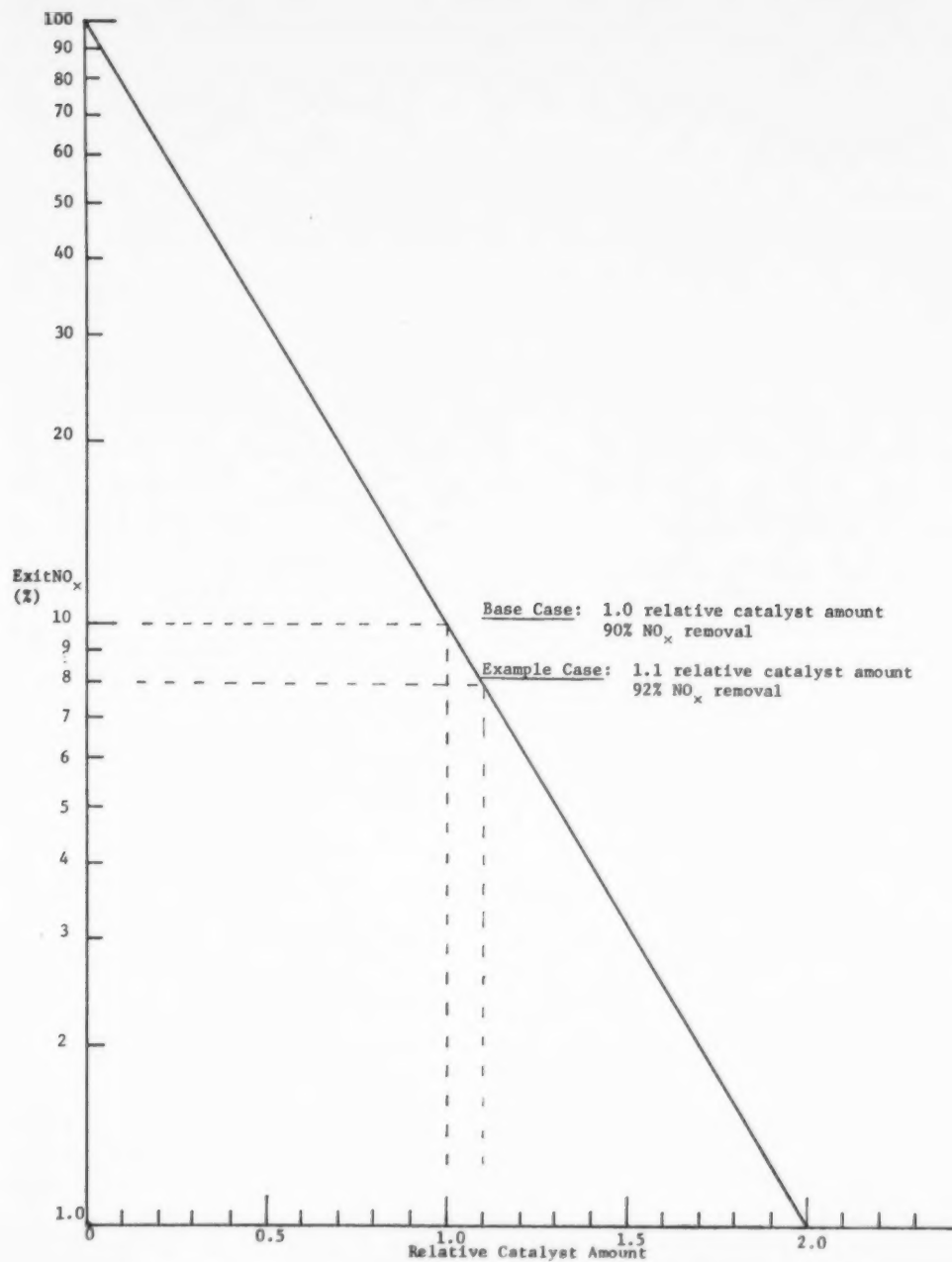


Figure C-1. Exit NO_x as function of catalyst.

that this amount of catalyst (with a 1.0 NH_3/NO_x injection ratio) lowers the outlet NO_x to 8 percent of its inlet amount. This is a 92 percent NO_x reduction. It is estimated that the NH_3/NO_x injection ratio could then be lowered to 0.98 and still achieve 90 percent NO_x reduction.

$$\text{NH}_3/\text{NO}_x = \left(\frac{90\% \text{ reduction desired}}{92\% \text{ reduction capable}} \right) (1.0 \text{ NH}_3/\text{NO}_x) = 0.98$$

The NH_3 emissions for the 350 ppm NO_x inlet basis are determined as follows.

$$(\text{NO}_x)_{\text{IN}} = 350 \text{ ppm}$$

$$\text{NH}_3/\text{NO}_x = 0.98$$

$$(\text{NH}_3)_{\text{IN}} = 0.98 (350 \text{ ppm}) = 343 \text{ ppm}$$

$$@ 90\% \text{ NO}_x \text{ removal, } \text{NH}_3 \text{ that reacts with NO}_x = 0.90 (350) = -315 \text{ ppm}$$

$$\text{NH}_3 \text{ that oxidizes (estimated 2\%)} = - \underline{7 \text{ ppm}}$$

$$\text{NH}_3 \text{ emissions } \approx 20 \text{ ppm}$$

To calculate the initial formation temperature of ammonium bisulfate in a gas stream containing 21 ppm NH_3 and 10 ppm H_2SO_4 , the expression for the equilibrium constant is used. (The expression is written in the terms of the bisulfate decomposition for calculational convenience.)

$$K = (4.60 \times 10^{-12}) (\exp [27,280 (\frac{1}{423} - \frac{1}{T})]) = (Y_{\text{NH}_3}) (Y_{\text{H}_2\text{SO}_4})$$

$$\exp [27,280 (\frac{1}{423} - \frac{1}{T})] = \frac{(21 \times 10^{-6}) (10 \times 10^{-6})}{(4.60 \times 10^{-12})}$$

$$\frac{1}{423} - \frac{1}{T} = \left(\frac{1}{27,280}\right) \left(\ln \left[\frac{(21 \times 10^{-6})(10 \times 10^{-6})}{(4.60 \times 10^{-12})} \right] \right) = 1.40 \times 10^{-4}$$

$$\frac{1}{T} = \frac{1}{423} - 1.40 \times 10^{-4} = 2.22 \times 10^{-3}$$

$$T = 450^{\circ}\text{K}$$

$$= 177^{\circ}\text{C}$$

$$= 350^{\circ}\text{F}$$

(The initial formation temperature at 30 ppm NH₃ and 10 ppm H₂SO₄ is 355°F).

Annualized Cost Summary

INCREMENTAL CAPITAL COSTS FOR INCREASED CATALYST CHARGE TO REDUCE NH₃ EMISSIONS

For 10 percent additional catalyst

Assume: Installation factor for both catalyst and reactor are equal

Reactor cost increases linearly with reactor size

From TVA report³: Installation factor = 1.41 x equipment cost
Indirect investment = 1.872 x direct investment

Incremental reactor capital cost =
\$1,029,000 x 0.1 x 1.41 x 1.872 = \$271,600

Incremental capital cost for initial catalyst charge
\$6,370,000 x 0.1 x 1.41 x 1.872 = \$1,681,400

Incremental annualized capital charges
(\$271,600 + 1,681,400)(1.46) = \$285,100

Incremental annualized costs for catalyst replacement

1 year catalyst life

$$\$6,370,000 \times 0.1 \times 1.41 = \$898,200$$

2 year catalyst life

$$\$6,370,000 \times 0.1 \times 0.5 \times 1.41 = \$449,100$$

APPENDIX C
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